Phosphorus in the Environment: its chemistry and biochemistry

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Ciba Foundation Symposium 57 (new series)

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Phosphorus: a general introduction

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This symposium report is an effort by a diversified group of scientists to look at a wide general problem which faces mankind: the proper use of the world's phosphate resources. This is not just a scientific problem; it has economic and political overtones. Some are obvious: for example, the need to supply phosphate fertilizers to huge areas of the earth at an economic price, and the prevention of pollution. Others are not so obvious, such as the risks and value of the use of organophosphorus compounds in combating insects and weeds. Since most of the participants in the symposium have little or no political experience little attempt is made in the articles to comment within political confines (i.e. 'within the art of the possible') but rather the authors have gone out of their way to present an accurate, although often simplified, version of their specialist knowledge.

The volume starts with papers on the magnitude of elementary phosphorus resources and man's demands for phosphate. There follow chapters on the way in which both inorganic and organic chemists look at phosphorus reactions in relation to biological systems and how phosphorus chemistry can be used to affect life in ways not open to biology. The knowledge is then used as a background for the examination of particular regional problems, usually of plant cultivation when phosphate is often deficient. A later section analyses the problems of excessive phosphate mainly due to sewage and detergents in other regions. Only in the final sections of the book are the political aspects touched upon, and then only in so far as they have already influenced events.

The general problems of the energy supply for the Western World have been presented time and again and yet the political impact of this knowledge is slight compared with that of the immediate economic and social difficulties. The supply of energy is one of many similar world problems which should be the subject of broad political discussion and action but which, as a result of

local personal and national aspirations, receive scant attention. A second such problem is the world distribution of phosphorus, an element which is essential to the world's food supply. It is not my purpose in this introduction to point out any of the details associated with this distribution or possible ways of improving it but to direct attention to the areas with which we are concerned.

First, the essential role of phosphorus in life should be understood. Biochemists understand this role and leave us in no doubt that there can be no substitute for this essential element. If we want higher yields of biological materials (food) we need a greater supply of phosphorus. The second piece of information biochemists can give us is that the cycle of phosphorus in biology (Fig. 1) may take millions of years to complete and in this way phosphorus differs from carbon, hydrogen, oxygen and nitrogen, which have much faster cycles.

rock → soil →plant → animal → sea → rock (sediment)

$\sim 10^6$ years
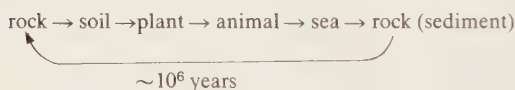
FIG. 1. Cycle of phosphorus in biology.

We can treat the distribution of phosphorus as a one-way traffic from rock deposits to the sea as far as events of biological importance to humans are concerned.

We then have to consider who 'owns' the deposits of phosphorus. If the phosphorus ores lie in the lands of one nation rather than another (as they do), then sooner or later phosphorus will become a governing currency. We need to ask about the cost of getting phosphorus in usable form for agricultural purposes and the way in which the price could be politically influenced. This raises questions such as 'Can nations on the Indian subcontinent afford enough phosphorus?' Not only the price but the technology is obviously important. Are there possible ways of getting phosphorus in a usable form from the ore at a lower price? To what degree is the price of phosphorus fixed by the price of energy?

The availability of an element is but part of the political problem involved in its distribution, for we could ask if it is sensible to try to meet demand. In phosphorus we have a tool with which to control population. Should we use it? It is no good hiding from these thoughts if the choice is starvation today or starvation tomorrow. Today we already allow areas of the world to sub-exist

while the Western World uses much phosphorus for purposes other than food but we do not declare that this is a deliberate policy.

Against this background we must review the passage of phosphorus through the soil/plant/animal system. Is this efficient? How much phosphorus goes straight through from rock to ocean? What can be done about it? Can we improve fertilizers or plants? Moreover, if the flow of phosphorus is not as we want it to be, we may consequently fertilize forms of life in rivers, lakes or seas which are of no direct value to us. This is called pollution. Can we control it? Or does our present agricultural practice inevitably build some food chains and destroy others?

The soil is not something passive in the passage of phosphorus from the distributed product to the plant. The soil interacts with phosphates and in turn this interaction affects the availability of other elements. Do we know enough of the chemistry of soils to be sure that present phosphate treatments are good and without side-effects? Even if food-yields greatly increase over the next 100 years we must try to avoid the possibility that at some future date these increases are shown to have been gained at the cost of the ruin of the land for an equal number of years. As with all of man's activities today we have to take a long-term look at their consequences. We cannot afford short-term attitudes.

Phosphorus is used not only in fertilizers but also in detergents, in which it acts as an essential water-softener. Through the use of detergents hygiene (health) standards are improved. But what is the other side of the coin? Does this use of phosphorus greatly increase pollution? Or is this a marginal effect? Can we get away from a washing procedure based on a phosphate water-softener? Here chemists can come back into their own by developing new products, for it is now not the case (as in the biochemistry of life) that there is no possible substitute for phosphorus.

However, whatever is said about the soap and detergent industry, we must not be so foolish as to press for changes in detergent standards if it is our agricultural and sewage systems that are the real causes of pollution by phosphate. To do so would be a foolish confidence trick on the public; in a drought one saves no significant amount of water if one mends a leaky tap but leaves the sluice gates open. Again we know enough today to state that the switch from a harmless bulk chemical product, phosphate (in say a detergent), to another type of bulk product could lead to a pollution disaster unless large-scale biological tests of the new product are made before its introduction. These precautions take time. We may have to alter our industrial practice slowly. Of course this implies a greater need to start correctly. There are other problems, which are not just technological, for there is great interest

in the use of phosphorus compounds as so-called pesticides and herbicides to control competitive life forms. Do we understand the chemistry and biology of these phosphorus materials sufficiently to be able to use them entirely safely or are we heading for consequences like those met with DDT? The organic chemistry of phosphorus, which is so deeply involved in life's own processes, is now deeply involved too in man's effort to control life in a discriminating way. Is it possible to see what the future holds here?

All of us at this symposium can see that through phosphorus chemists have learnt to interfere strongly with natural processes. At first the scale of this activity was such that it was of no great matter. In recent years, however, the food supply of the world has become linked with man's uses of this element. A primary task of scientists is to present this problem in an intelligible form. I believe that there are other tasks. The role of chemists and biochemists in society must change and must change quickly. They have to become high priests—not leaders; people with information, perhaps seemingly mysterious, who are there to be used to the advantage of people generally. We must form a larger part of the civil service. We then have a third task which is to see that students of chemistry are not educated just to describe chemical systems but to be aware of the effect added chemicals may have on the ecosystem. I hope that this symposium on phosphorus will lead the way to these ends and can be followed by similar symposia on other elements such as sulphur and chlorine, with which similar problems arise.

Furthermore, I hope that this symposium will inform a wide range of readers and make them aware of the benefits and disadvantages the use of phosphorus confers. Governments today must be advised about environmental issues, for instance, before these issues become critical problems. Especially in democracies safe decisions can only be made if the supply of information allows 'eternal vigilance'. The contributors to this volume hope that it will be used as such a source of information.

Phosphorus and mankind's problems today

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Abstract   The unprecedented increase in the worldwide population of humans—a growth which has been underway for two centuries and has been continuously accelerating—seems to be a root cause of many of the problems of today, including those treated in this symposium. Current events once more arouse fears that the probable conclusion of our present growth era will unfortunately consist of widespread death from famine, pestilence, and social disruption of various kinds (perhaps involving nuclear devices). Non-local efforts to avoid famine induced by rapid population growth seem only to delay an eventuality that will thereby finally lead to many more people starving. In this paper, phosphate pollution and soil erosion are treated as indirect results of the population boom; and some radical changes in soil and water management are suggested for lessening these problems for large populations.

PHOSPHATE ROCK AND THE FUTURE OF MANKIND

As part of the numerous large-scale changes that we humans have introduced into our lives during the past 100 years there has been a growing worldwide use of plant fertilizers obtained from mining or chemical operations or both. A key mineral-based constituent of fertilizers is phosphorus (usually as an orthophosphate salt), which is one of the three elements (nitrogen, phosphorus, and potassium) that are emphasized in fertilizer technology. Phosphorus is concentrated (in the form of apatite minerals) in relatively few large deposits that may be mined and used commercially without an unreasonable demand for labour or energy resources. Most of this phosphate rock ends up in fertilizers; and deposits that appear by present standards to be economically feasible to mine are expected to last for the next few hundred years. Because of its central role in both photosynthesis and the metabolism of all known forms of life, phosphorus is a key element for all life on earth.

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In view of the large and rapidly growing human population of the world, many optimists look to a greatly increased use of chemical fertilizers as the means whereby the vast hordes of mankind expected in the next 25–100 years will be enabled to feed themselves. Implicit in this point of view is the pious expectation that at some future period the world's birthrate will be voluntarily reduced so that the population will become stabilized at a level presumably far greater than that of the present. Indeed, it has sometimes been implied that a combination of chemical fertilizers, new strains of food plants with improved yields, and the continuation of 'high technology' based on abundant supplies of energy and water will allow nearly everyone in the so-called 'developing' regions to be well fed and to enjoy consumer products such as are now available to the moderate-income inhabitants of the technologically advanced countries. On these assumptions (or variants of them), careful use and conservation of the easily mined phosphorus deposits could become a sacred trust for the future teeming generations. In brief, this trust might be embodied in a proposal for mining no more phosphate rock than is necessary for sufficient food production and using it in such a way that dissipation of phosphorus into run-off waters is minimized.

Although the above scenario for the future is not impossible, it seems unlikely, being based on a delusion of grandeur that was common currency in the second quarter of the 20th century, when the media often reflected a science-fiction view of unlimited future aggrandizement for mankind. The present-day emphasis on an ecological scheme in which the human has his niche, with natural limitations for all creatures, seems to be a healthy anodyne to that recent wave of undue arrogance. As I see it, the importance of chemical fertilizers to the future of mankind depends very much on the resolution of the population-growth phenomenon and to some extent on the availability and apportionment of energy in the future. Therefore, I shall touch on these matters below.

THE POPULATION EXPLOSION

Archaeological and historical evidence shows that the total human population of the world has until the past few hundred years consistently been small, with near-zero growth rates (Ehrlich & Ehrlich 1972; Coale 1974). There have, of course, been pronounced local fluctuations in population during this time, as evidenced by the various 'lost' cities in jungles and deserts and certain large-scale migrations of people. However, in the past few centuries the world population has grown faster and faster. Thus, in 1650 the total population was about 500 million people and it took about 200 years for

it to double. The next doubling of the population (from around 1000 million in 1850 to 2000 million in 1930) occurred in 80 years. The succeeding doubling time, which brought the world population to 4000 million in 1975, was only 45 years. Extrapolation suggests a population of 8000 million people in about 35 years (i.e. around 2010 A.D.). At present, the increase in population corresponds to about 200 000 additional mouths to feed each day! Obviously this rapid increase in the rate of population growth (a 1000-fold rise from 1700 to 1970) must cease or there will simply not be enough land left on earth to contain the human masses, much less to maintain a food-production system to feed them.

From the plot of the percentage rate of population increase over several millennia in Fig. 1 (Freedman & Berelson 1974) it should be clear that this rate must drop back to zero or below sometime in the more-or-less near future if there is to be sufficient space to support the people. As may be inferred from Fig. 2, the exact shape of the right-hand side of the peak shown in Fig. 1 will determine the future world population level. A particularly horrible situation would be a future alternation of positive and negative rates of world population, averaging out to zero or negative growth rates, as could happen if there were occasional widespread nuclear devastations or other large-scale periodic disasters spaced by at least several generations.
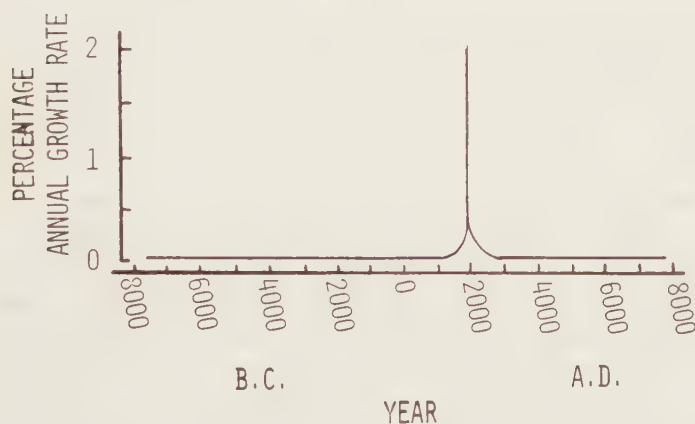
FIG. 1. A graph showing the annual growth rate of the human race as a function of time over 16 000 years. Until recently the average annual growth rate for the world was close to zero and it must return to this value in a short time (on the scale of this graph) in order that there be sufficient room on earth to support the human horde in any condition sufficient to sustain life.
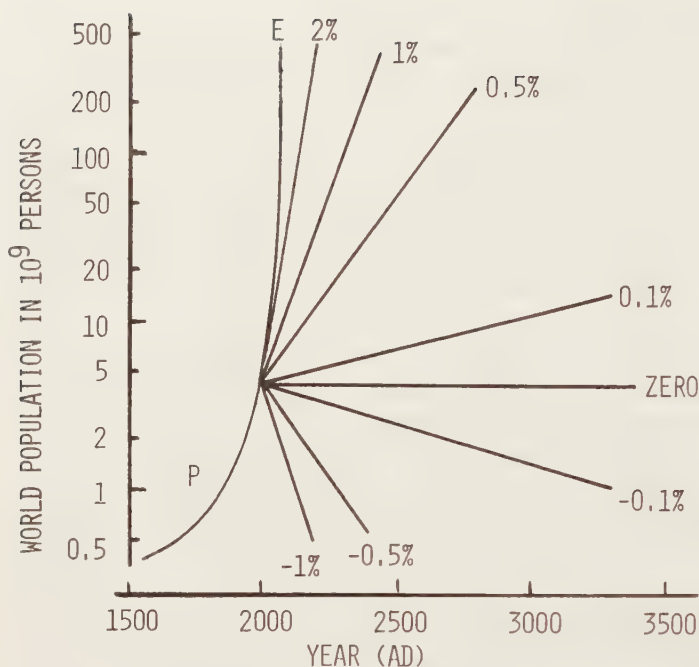
Fig. 2. A plot of total world population in terms of 1000 millions of persons (on a logarithmic scale) against time (from 1500 to 3500 A.D.). The section of the growth curve labelled P corresponds to the observed population increase to date. An extrapolation of this curve into the future is labelled E. Other extrapolations are made, assuming the noted, fixed, annual growth rates (in population percentages). The line for zero growth rate corresponds to maintaining the present population, and those for negative growth rates correspond to population losses.

When the ratio of the birth rate to the death rate is unity, the corresponding rate of population growth must be zero; an increase of this ratio above one corresponds to a growing population (assuming no inward or outward migration, as must be true for the entire earth). Around 1750 in England, the annual death rate per 1000 people (the 'fractional' death rate) started to drop precipitously from a value slightly below the fractional birth rate, which did not begin to drop similarly, however, until about 100 years then passed. Indeed, only in the past few years has the ratio of birth rate to death rate in England dropped close to the current value of unity.

As the industrial revolution spread so did the population boom, so that the developing countries are now in the midst of the social processes involving dropping death rates and unchanging or slightly increasing birth rates. Fortunately, England and then the rest of Europe in their period of high popu-

lation growth had the thinly populated areas of the Americas and Australia in which to expand; and the spread of colonialism elsewhere also drew off some of their excessive populace. To settle the West, a high birth rate was also advantageous in North America for much of the period of expansion. Such ready dispersal of people is no longer possible so that the areas now experiencing rapid population growth must face the trauma of supplying jobs and food for the additional populace (Demeny 1974). As a result, the truly magnificent increases in agricultural and industrial production being made in the developing countries are continually being swallowed up by the additional population so that there is little or no improvement in the lot of the average person.

Much of Asia already has a high population density in the arable regions, often coupled with a high growth rate. This situation is also found in some parts of the Near East and in North Africa. South America and Black Africa on the whole have not had excessively large populations but their growth rate is fast so that this situation is changing rapidly (Anon 1976).

SOME FACTORS OF THE POPULATION INCREASE

The decline in the death rate which leads to an imbalance of the numbers of births and deaths is often attributed to applications of modern medicine and/or the use of synthetic pesticides. However, when the population explosion started in Europe, medical treatment consisted predominantly of blood-letting to remove evil humours, and leeches were commonly used for that purpose. At that time as well as today, simple factors resulting from socioeconomic changes seem to play the important role—factors such as cleaner surroundings at childbirth (sheets, not dirty straw), less contact with vermin (owing to better housekeeping and improved personal hygiene), and minor household improvements (workable chimneys, more cloth [and now plastics] available for use, better water supplies, *etc.*). Partial substitution of easily washed cotton for wool cloth was a significant factor in Europe.

Lowered death rates alone are not sufficient to explain the population boom which has accompanied the spread of the Industrial Revolution, in view of the fact that mankind has traditionally had many methods for controlling births and that additional methods are still being developed. The traditional methods (Himes 1970) include (1) abstention, (2) forms of sexual release not involving penetration of a woman by a man, (3) various special modes of sexual intercourse that inhibit conception, (4) use of a range of simple sperm barriers or naturally-occurring spermaticides, (5) crude surgery, often of an ingenious nature, (6) female barrenness due to extended suckling of a child, as

well as (7) abortion and infanticide. For example, an intriguing birth-control procedure formerly used by native Australians consisted of forcibly ejecting ('spitting') sperm from the vagina by means of a form of muscular control taught to young girls (see, e.g. Mantegazza 1932). Sociological studies in various parts of the world have shown that couples on average have the same total number of children that (in accord with the local conventions) they planned to have when they married (Berelson *et al.* 1966; and for specific studies, Dow 1967; Heisel 1968; Caldwell 1969; Masters & Iraka 1970). In other words, the present high rate of population growth seems to be due to choice based on sexual traditions, regional customs, and commonly held local expectations about the impact of children on the living standards of the family. Since social transitions must usually overcome considerable inertia, the traditional strictures that formerly resulted in a stable population are not easily changed when simple technological improvements reduce the death rate; the birth rate continues at a high level until changing conditions favour a return to population control or the need for this return becomes generally perceived. Only then will the lengthy and often halting process of suitably modifying the codes of sexual behaviour finally take place. Unfortunately, the necessary time and resources may not be available for this relatively peaceful process to take place, so that there is a strong possibility that the resolution of the present world population boom will be widespread death and destruction.

EFFECTS OF THE PRESENT-DAY OVERPOPULATION AND OVERCONSUMPTION

The present situation with respect to the growth of the world population is unique in the history of mankind (Ehrlich & Ehrlich 1972; Freedman & Berelson 1974). Moreover, the worldwide network of communications has knit together the strands of our diverse cultures to an unprecedented degree so that in may respects we are all in the same boat. Therefore in our search for a parallel to our present situation among other animals, it would be nice to find a situation in which a mammalian species existed in a circumscribed benign environment in which it had plenty of food and no predators. Although this situation applies in the wild only to a few slow-breeding predators at the top of their food chains, the introduction by humans of a fast-breeding species to a suitable new locality may lead to a rapid population explosion. The consequences of such an action are illustrated by the following story of the release of rabbits in 1903 on two isolated Pacific islands in the Hawaiian chain (Lisianski and Laysan) as a potential source of fresh meat (Watson 1961; Anon 1962). Not long afterwards, the local guano workings were abandoned and nobody was around to hunt the rabbits.

By 1913 the vegetation on the small sand and coral island of Lisianski had been completely destroyed and only a few rabbits were still alive. A 1923 expedition found that the only remains of the rabbits were some bleached bones and that plant life was starting to regenerate. The story was similar on the larger, more verdant island of Laysan, where vegetation damage by the rabbits led four men to spend three months on this island early in 1913 to kill off the rabbits. Although over 5000 were slain, some rabbits survived. They and their descendants had reduced the island to a barren waste by 1923, at which time the few hundred surviving rabbits were hunted and killed. Several species of rare birds native to Laysan died out because of the chaos due to the population explosion of the rabbits, and the original lush groves of trees had been destroyed to the point that only four stunted trees were left on the entire island. In 1936, the island was again covered with vegetation and by 1949 the black-footed and Laysan albatrosses were reestablished.

Mankind is well on the road to reducing the entire world to a barren waste, just as the rabbits destroyed their little worlds of Lisianski and Laysan. We humans, with our extensive material possessions and our magnificent ability to produce refuse and rubbish, offer a threat far beyond that of an equal number or weight of any other animal. The present concern about pollution, dwindling resources, and the destruction of whole species of animals is a small sign of recognition of the course which we are following in which the richer countries (particularly the USA) are geared to overconsumption while the poorer ones are burdened with overpopulation. Obviously an average individual in a country with high gross national product causes much more environmental degradation than one in a poor country. I suspect that the average destructive impact per person increases more-or-less logarithmically (rather than linearly) with gross national product. The high population with respect to the arable land in many of the poor countries also represents a powerful force leading towards destruction—a situation that is exacerbated by the desperation of the very poor which allows no surcease in the pressures on the land.

People living in areas of high population density can exist in long-term equilibrium with the land without appreciable ecological damage; but a rapidly growing population has little chance of attaining this state because of ceaseless struggles to support the newcomers. I do not see how the rapidly-growing poorer countries can possibly fulfil their aspirations for 'development' while maintaining their present birthrates. In any event, soil erosion and other factors converting arable lands into wasted areas continue relentlessly while more and more supporting territory, such as swamps and forests, are converted into farm-land. The problems of soil erosion and other forms of

land degradation are not restricted to the developing countries. The USA and Canada in their role as providers of food for the rest of the world are experiencing erosion of the soil by water and wind at a much higher rate than is at all consistent with permanent agriculture (see, e.g., Brink *et al.* 1977).

Western culture has become extremely dependent on fossil fuels (especially oil and gas) in order to keep going. These resources are, by their very nature, limited; and the world is expected in the near future to be faced with an energy crisis that is physically rather than politically determined. Energy sources that are now little used will be developed, but at costs far exceeding those that have been involved in obtaining oil and gas from existing fields. Solar energy holds promise, although its widescale application may lead to major changes in the economic capital structure as well as in the daily habits of the extensive users of energy. The recent large increases in the price of oil have placed an especially heavy burden on the poor countries with rapidly increasing populations. Among other things, they have led to lessened availability of chemical fertilizers and of fuel for irrigation pumps.

POLLUTION BY PHOSPHATES

In general, all mammals behave destructively toward their environment, and modern humans are particularly adept in this respect because of continual replacement of their material possessions and their widely ranging activities. However, even the archaeological sites where primitive man lived are characterized by the large amounts of refuse they contain. Obviously, the larger the population and the higher the level of affluence, the greater is the impact on the environment.

With respect to water pollutants that act as plant foods (such as the phosphates), a serious source of trouble lies in our common modern practice of destroying swampland through its conversion for agricultural or residential purposes. The much-cited case of Lake Erie on the Canadian–USA border (Anon 1967) is a prime example. The western half of this lake is an extremely shallow portion of the Great Lakes' system and is fed by a group of swampy slowly-moving rivers in addition to the flow from Lake Huron. In the early days most of the shore of western Lake Erie was bounded by the Great Black Swamp (Hatcher 1945), which acted as a filter for the natural fertilizers and the sediments brought in by the rivers. Nearly all this swamp was drained by the settlers so that the suspended matter (augmented by the agricultural activities) now flows directly into the lake. As a result the original fish, such as lake trout and muskellunge, have been slowly replaced by less desirable species, such as sunfish and carp, since many of the original fish need clean

stones on which to lay their eggs. When these stones became covered with silt, the eggs were doomed to destruction. At the same time, the plant nutrients, which had supported the swamp, now readily passed into the lake along with the added nutrients resulting from the practice of agriculture.

Urban concentrations, such as Toledo, Ohio, were built beside the lake in areas that were formerly all swamp, so that there were no natural filters (the swampy lands) left to soak up the cities' effluents. Crude evaluations of the concentration of green algae have been made in western Lake Erie for many years by measuring the depth at which a submerged white disc may still be perceived (the Secchi-disc measurement). These measurements indicate that eutrophication has been proceeding gradually, starting long before automobile manufacturing converted Detroit (at the head of Lake Erie) into a large industrial centre, often blamed as the chief cause of the algal growths.

A strong emphasis in agricultural research has been placed on the development of high-yielding strains of crop plants, which incidentally need to be fed unusually large amounts of water and fertilizer (Wade 1974a, b). As a result of this and other economic pressures, modern agriculture uses more fertilizer than is needed simply to replace the nutrients removed by cropping. This is exacerbated by the modern practice of not returning the inedible portions of the crop to the land, by composing and mulching, or by burning the wastes in the field. Since it appears that phosphate is transported from land to water primarily as adsorbed material on soil particles and as part of microorganisms rather than as dissolved salts, a suitable form of mulching and soil building would probably greatly reduce the transport of phosphates by water run-off.

Thomas Crapper's invention of the water closet in Victorian England was rapidly adopted across the world and has replaced the traditional chamber pots and privies. This along with modern agricultural practices has led to much of the phosphate pollution of surface waters. Now we think in terms of removing the sewage from the water in expensive disposal plants, when it would make more sense not to have put the sewage in the water in the first place. The process of composting human and animal manures along with vegetative waste is an ancient one which deserves more attention in modern Western culture. In much of the East, traditional methods of composting are extremely important and have allowed continuous agriculture to proceed for millennia (King 1911; Howard 1947). Conversely, present-day agricultural practices in the USA and Canada are not conducive to long-term agricultural use of a given piece of land (Albrecht 1975). Surely a strong emphasis on developing economical up-to-date methods of (1) composting manures and organic wastes (Satriana 1974) and (2) suitably mulching to minimize agri-

cultural losses of phosphorus could be an important avenue to success in reducing phosphate pollution to acceptable levels.

The use of phosphate adjuvants in washing compounds has been the subject of much criticism and some restrictive legislation. However, much of the problem is that more washing is being done today than before World War II, when these additives gained wide acceptance. For example, not only are articles of clothing, such as undergarments and shirts, being changed several times more often on the average, but washable permanent-press wear has been substituted for many items that used to be dry-cleaned rather than laundered. With the present amount of washing, a return to old-fashioned laundry soap would have deleterious environmental effects, particularly in hard-water areas where the river banks would be caked with insoluble calcium soaps. Recent test marketing of finely-divided zeolites as detergent builders raises the question of whether these materials will sequester too much of the essential minerals from surface waters. The polyphosphates undergo such rapid enzymic hydrolysis to orthophosphate that sequestration in surface waters has been no problem. An acceptable phosphate substitute should also undergo degradation to a non-sequestering form.

WHAT THE FUTURE MAY BRING

Neither technology nor our available resources can continue to cope with the increasing population for long. Indeed, it seems ethically undesirable to supply other than locally grown foodstuffs to feed the additional 80 million mouths that are produced each year by our fertile species, since it seems foreordained that a continued increase of the food supply without a halt in population growth will result in a vast increase in death and suffering when the time inevitably comes that food requirements can no longer be met. This time may nearly be upon us, since it is claimed that roughly one quarter of the people in the world go to bed hungry each night and more than that number do not receive adequate nourishment. Since few people in the countries having high rates of population increase appear to realize their predicament and no one seems able to ameliorate it, it appears likely that excessive human fertility will be conquered only by famine, pestilence, war, and/or general disruption or disintegration of society.

Perhaps a period of chaos is forthcoming, during which nuclear devices may play a role. This may bring about another Dark Age; but, if it does not, there is hope that we humans may then have learned through hard experience how to use technology without getting into too much trouble. (By the way, it may be impossible for humanity to escape from another Dark Age, which

would probably be worldwide, since we have nearly depleted the mineral resources of sufficiently high quality and ready availability to be used by an unskilled population. If this were true, humanity would then forever after be condemned to a bucolic existence—a not unpleasant prospect, assuming a tolerable burden of radioactive fallout or other noxious residues.)

In view of these speculations about the future, what attitude should be taken with respect to the use of phosphorus? In answer, I think that in the long-term whatever is done about the use of phosphate rock is unimportant; in the short-term, it seems advisable for the good of all mankind (regardless of race, country, or economic status) not to support population growth by any means (including phosphate-based fertilizers) in geographical areas where little or no attempt is being made to check this growth. Likewise phosphorus chemicals should not be used to support overconsumption, so that the environment need not be degraded frivolously.

Since widely used technological innovations soon become keystones of the economy, the suggestions made above with respect to the management of soil and water (as well as the broader topics of curbing overpopulation and overconsumption) cannot be undertaken lightly for fear that clumsy removal of these keystones might topple the structure. However, it seems desirable, in view of the magnitude of the challenge, to aim at attacking these problems directly instead of emphasizing short-term and minor repairs to the social and economic system, regardless of their long-term effects.

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Discussion

Tinker: Continued increase of the world's population implies that some resource will finally be exhausted. Is there any evidence that phosphate will be the critical one?

R. J. P. Williams: The issue is rather how we use phosphorus now so as to avoid any possible crisis. A parallel exists with oil supplies. One could argue that in view of the limited reserves of oil we should immediately move away from a technology based on oil. Similarly one could argue that fertilizer habits should be changed now. By controlling the distribution of such chemicals—phosphorus, oil or whatever—we can control development, even of population. Dr van Wazer is interested in the control of the distribution of phosphorus, urging us not to keep on mining the ores if we can avoid it—to do so is uncontrolled development which will certainly lead to a rapid increase in the population. Rather we should revert to alternative methods of fertilizing land and produce less food, his implication being that the increase in the population would not then be so fast. I don't know whether the second statement is true or false.

Tinker: Does this imply that we can stop the population explosion by ceasing to use fertilizer phosphorus and thereby produce famine?

van Wazer: Non-local efforts to avoid famine induced by rapid population growth seem only to delay an eventuality that will finally lead to many more people starving. That is my perceived reality.

Tinker: That recalls the argument about the Irish potato famine, namely that, if agriculture were improved or rather if food were brought in from outside, the problem would worsen because people would survive the famine into the next year when the problem would be exacerbated. This Malthusian approach is a very hard-line one which most people nowadays would agree was a mistake. (In the UK we are still living with the problem that was started then.)

van Wazer: But the Irish emigrated to America at a great rate for a long time. That is how the problem was handled.

R. J. P. Williams: Are you saying that Malthus was wrong?

Tinker: I do not see how one can control the population in that way without producing the very catastrophe that Dr van Wazer has prophesied. It is just another way in which the catastrophe can occur. We are looking for a more controlled way, whereby agricultural improvements stave off famine, while somebody tries to find another way of controlling population. I don't see how we can in practice control population through the supply of phosphorus.

Brinck: Saying that we should produce no more phosphates to feed the people who already exist is a very one-sided action. Who will die first? The people who need food most—not those in the developed countries, who could continue producing food. If one raised the price of phosphates, the under-developed countries would no longer be able to buy as much as they used to. We should be more concerned with education for birth control than with regulating the supply of raw materials.

Shaw: Population control—a politically explosive subject, as recent events in India have shown—is vital in the long term but first we must educate people that birth control is not only desirable but essential. That will take time; social and biological memories (traditions) are long. Progress cannot be made in only a few years unless force is used, and that can lead to disastrous consequences. In the meantime, agriculture ought to make the necessary impact to fill the gap.

Kabbaj: Rather than the use of phosphate controlling the population increase the reverse is happening: the increase in population controls the use of phosphate rock through technical and economic factors. The increase in population is the consequence of many other factors besides the use of phosphate and cannot be controlled through only one of these factors.

McClellan: I should add that phosphorus is not the only critical element in the production of food; by and large it is nitrogen. There is almost an order of magnitude difference in the impact, particularly in areas where the population density is high. In areas of Asia (Japan, Philippines, Indonesia, Bangladesh, etc.) rice is the principal food staple. Rice seldom shows much response to phosphate but often shows a large response to applied nitrogen. This is true also in Africa and Latin America.

Brydges: Dr van Wazer, you referred to the decline in the death rate. Aren't we approaching a time when it will increase again? Aren't we delaying the inevitable? Most of our population now die at a much later age than many years ago.

van Wazer: Yes. As I mentioned (p. 15), in many respects one of the most unethical things that we can do today is to continue over a period of years to

supply foodstuffs grown elsewhere in the world to support rapidly growing populations in areas where they cannot properly support themselves. On the other hand, efforts to help people to feed themselves are advantageous to all, although probably not as valuable as an equal degree of effort directed towards birth control. Let me add that I am not talking about special emergencies, such as earthquakes and unusual floods.

Reynolds: In countries whose growth rates are low or maybe negative we are in danger of becoming complacent. The UK, for instance, is still one of the world's richer countries with a *per capita* consumption of resources that is much higher than that of nations which are less developed and still have positive population growth. Our problems are not over; we still depend on other countries.

R. J. P. Williams: It would be interesting to know whether the consumption of phosphorus in the UK is still increasing [see p. 47]. Even if our population is not increasing, our standard of living may create a greater throughput of phosphorus. As I understand Dr van Wazer, we should cut off the path I mentioned for phosphorus (p. 2) from rock to soil by reducing the amount of phosphate being distributed in the world, encouraging the agricultural industry to work with less phosphorus, rather than increasing the flow of phosphate which, he says, will inevitably lead to an increase in population.

van Wazer: No; it seems to me that most people working in technology and science tend to work on the 'quick-fix' approach when we ought to be taking a long-term view, if possible. We ought to consider the social effects of our innovations, especially as we have been using mined phosphorus for only about 200 years, and mostly in the past few decades. The way humans get rid of rubbish (trash) and bodily wastes is an important factor in the overall phosphorus balance. Do we really want our present technological 'fixes' to these problems?

Emsley: The desire to live in cities seems to summarize your worry. Referring to Professor Williams' diagram I get the impression that you would like to reverse the flow of phosphorus from plant to animal and take dung back to the land. But as we tend to congregate in cities we have to flush our excreta away to make life bearable.

van Wazer: There is no need to flush it away. Some people use non-water-closet toilets in which the faecal matter passes to a place where it decomposes, producing gas. In some of these units the solid material is dried (a high-energy operation) to an odourless material which can be returned to the land. There are several such interesting possibilities but practically no money is put into research into them.

Emsley: That is all very well, but the capital investment that has gone to

improve, for example, the quality of the river Thames by sewage treatment is so enormous that I don't see how we could ever turn to such things as local methane generators. Without altering the character of our cities we cannot change the present arrangement.

van Wazer: It is easy (as in research projects) to raise arguments about why a proposal will not work. All I am saying is that people have not thought sufficiently about these matters. Money could be put into such studies.

de Oude: Urbanization is not the root of the problem; similar problems have to be faced in agriculture when inappropriate practices are used. Phosphorus in cattle-feed, enriched with more phosphate than cattle can take up, may equally be lost from the recycling process.

On the other hand, cities without sewers do not necessarily have these problems. A very readable book by Slicher van Bath (1976) on the history of agriculture records a 1812 travelogue which reports how barges transported the waste from the cities in Holland to Flanders where it was used as manure. Thus, the problem results from the social behaviour that society accepts or demands, not just from urbanization.

Larsen: The water closet is no novelty; it was introduced into England during the Roman occupation.

van Wazer: Thomas Crapper's invention was the trap that kept the gases from coming back into the room and the sewer vent that goes out through the roof. Before that time, indoor toilets that led into a sewer stank so strongly that people did not want them in their houses and hence it was more convenient to have a backhouse.

Bowman: Increases and development of populations in rural areas with an almost self-sufficient reliance on agriculture will lead to the recycling rather than the loss of phosphorus. In contrast, urbanization will need food to be moved from rural areas into urban areas; the phosphorus will not be recycled for food production and the demand for phosphorus will probably increase.

van Wazer: In the USA many people live in suburbia, where the sewer systems are still being extended. People who are coping well with septic tanks will now, by law, have to be connected to the sewer when it reaches them. This seems to me to be an expensive step in the wrong direction. Is this merely social habituation or is it a true need for such dispersed communities? Obviously a large city is a different story.

Bowman: But even in suburbia the phosphorus is not being recycled unless the sewage sludge is being spread on agricultural land. The contents of septic tanks are usually emptied into local treatment plants and so add to the total urban sewage.

Brydges: The Ontario Ministry of the Environment has recently observed

during routine monitoring that, as a consequence of septic tanks being emptied into ground water, the water resources were being contaminated with nitrate.

Larsen: Professor Williams could have quantified his scheme (p. 2). During the beneficiation of rock phosphate half the phosphate may be lost. When fertilizer phosphate is added to the soil, the amount of fertilizer P removed by cropping is reduced by a factor of 10. Then, in going from plants to animals it is further reduced, and similarly from animals to faeces. Thus it is not possible to sustain the phosphorus cycle by collecting all the faeces and returning them to the soil.

R. J. P. Williams: So my scheme (see pp. 2 and 284) should show that one part in, say, 10^4 of the mined phosphate appears at the end in the animals and that before it reaches plants 90% of what we take from the rock stays in the soil or ends up in water but most of the 90% is in the soil where it stays for a very long time.

van Wazer: How much enters the water from the soil, from plants, and from animals?

Larsen: Soil erosion is important. Most of the phosphorus entering the waterways comes not from fertilizers but from soil, owing to erosion.

By talking about plants, we normally refer to plants that can be eaten by either animals or man. Other plants may also be important, i.e. trees. For instance, in Finland next year 2×10^5 hectares (ha) of land will be fertilized for timber production with chemical fertilizers, mainly phosphorus.

Shaw: The Tennessee Valley Authority is experimentally fertilizing trees with slow-release fertilizers from the air, and that probably needs to be done only once every seven years or so. Slow, controlled release of fertilizer might enable us to cut the loss of available phosphate by using more and misusing less of the phosphate added to the soil.

Larsen: Slow-release materials may be of benefit for nitrogenous fertilizers. But when even a water-soluble phosphate enters the soil it becomes a slow-release fertilizer.

Granulation of fertilizers has been a technical breakthrough (see Dr McClellan's paper) but has made no impact on the recovery of plant nutrients. As an agricultural crop takes up 90% of its plant food within five or six weeks, there is no place for slow-release fertilizers except for particular cases.

McClellan: Most of our experience of slow-release fertilizers comes from temperate climates; little information exists for tropical soils in tropical climates. We still have much to learn since these are the only potential areas of arable land that are not presently under intense cultivation.

Arthur: To improve the efficiency of phosphorus fertilizers, we should try

to modify the competition between the soil and the plant for the phosphorus. This is not impossible in principle; one might devise a new phosphorus carrier which improves that competition as far as the plant is concerned by a mechanism of more direct fertilization.

Larsen: I have often wondered why phosphate deficiency in man does not reduce the birth rate, as my veterinary colleagues tell me that the fertility of cattle and their reproductive system are very sensitive to phosphate; when phosphorus is kept at a low level, the probability of conception is less.

Pirie: Ruminants can survive on extremely low-phosphorus or phosphorus-deficient material (straw, for example). People never eat food which is thoroughly phosphorus deficient except sugar and fats—all our other foods contain a reasonable amount of phosphorus.

van Wazer: Incidentally, zinc deficiency apparently causes such effects in humans (see Prasad & Oberleas 1976).

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World resources of phosphorus

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Abstract The geochemistry of phosphorus and the global distribution of its resources are reviewed. The concept of reserves and resources is discussed in view of recent price developments in the phosphate mining industry. A description is given of the application of a model called MIMIC (Mining Industry Model for Inventorization and Cost evaluation of mineral resources) for estimating the inferred global reserves and resources in different cost categories.

Based on the size and growth rate of annual production, the inferred reserves can be estimated at ± 20 000 Mt of phosphorus. This figure is in reasonable agreement with conventionally estimated demonstrated resources.

Estimates of exploitable resources with the MIMIC model vary between 40 000 and 500 000 Mt with about 20 000 Mt in deposits containing about 14% P (70% BPL).

The inferred reserves alone would satisfy current consumption for many hundreds of years. In this context, the historical growth rate of slightly less than 7% per annum appears neither exceptional nor particularly alarming with respect to the next doubling of the world population.

Phosphorus ranks about 10th in abundance of elements in the earth's upper crust. Its average concentration in this environment has been estimated at 0.1% by weight. Soils usually contain less than this especially when they have been extensively cropped or leached by acid ground waters (as in tropical countries). A phosphorus deficiency in soils is an important limiting factor for the growth of plants. Therefore, even if the element is not scarce in an absolute sense, its availability for the production of fertilizer deserves attention. For this purpose the element is non-substitutable; its use is dissipative and absolutely essential to life. Blakey (1973) has estimated that annually the equivalent of 20×10^6 tonnes (20 Mt) of commercial-grade phosphate rock (about 2.8 Mt P) are removed from soils by cropping. Although phosphorus resources are large by all standards, the timely supply of phosphates may become a limiting factor for agricultural production in the long term. With 80% of phosphate production going into fertilizers, the production necessary

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to feed the world population has increased at a rate about 2.7 times the rate of population growth (Gabor & Colombo 1976). Other uses of phosphorus include the manufacture of soaps and detergents (about 7%), animal feed, food products and medicines, electroplating and polishing of metals, its use in the petroleum industry, for military appliances and for many other purposes.

Substitutes for non-agricultural purposes, especially detergents, have been identified. Their application and market penetration appear to be mostly a matter of pricing and resources policy.

TERMS AND DEFINITIONS

There are several interrelated aspects to the problem of mineral supply: the natural availability of different materials; their geographical and geopolitical distribution; the cost of their extraction, concentration and transport; and the production capacities and potential of mines and fields. The classification of naturally-occurring materials into resources and reserves is an attempt to catch these different aspects under the common denominator 'weight of available product' for any given (or imagined) market or economic situation.

Most modern classifications are based on the recommendations of Blondel & Lasky (1956) on behalf of and approved by an international committee of the Society of Economic Geologists. In their terminology, 'reserves' is limited to estimated quantities of mineral materials considered economically recoverable with existing technology (i.e. exploitable), whereas 'resources' represent reserves plus all such materials which might become economically recoverable in more favourable conditions. Extensions of the Blondel–Lasky classification by the Commission of the European Communities (1972) and by both the US Geological Survey and US Bureau of Mines (1973) have emphasized that, in defining and appraising resources, two prime factors must be considered:

(i) the degree of geological assurance of their existence and magnitude (quantitative aspect);

(ii) the feasibility of recovery in existing economic and technological conditions (qualitative aspect).

The Venn diagram in Fig. 1 illustrates the Commission's classification, which closely follows the Blondel–Lasky terminology. 'Resources', however, here are defined as *all* naturally-occurring mineral concentrations in a given geological environment (= resource base), irrespective of economic considerations. The 'identified resources' of the USGS–USBM (1973) classification correspond to the 'potential reserves' (i.e. estimated exploitable plus '(para)marginal' plus 'submarginal' resources).
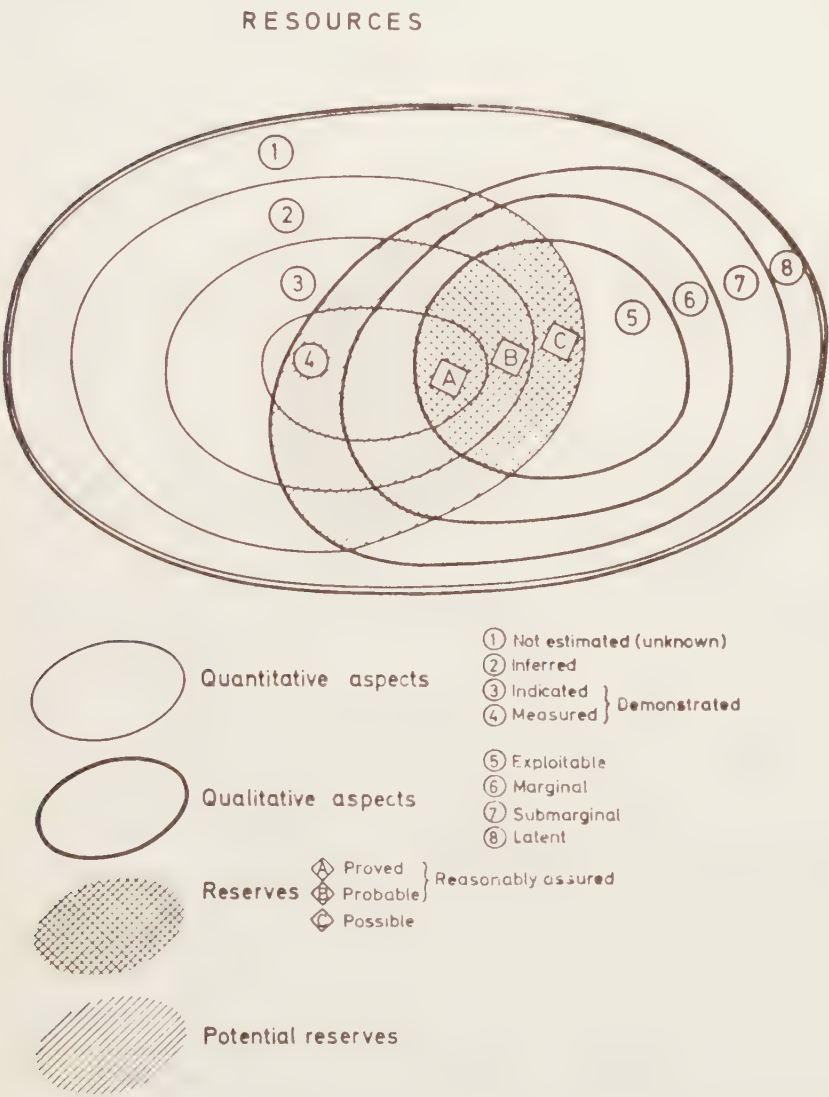
RESOURCES

FIG. 1. A Venn diagram showing the Commission of the European Communities' (1972) classification of mineral resources and reserves.

In the phosphate mining industry, the term ore (or matrix) is used to designate phosphatic material of mineable grade in place. If the phosphorus content, either originally or through upgrading, exceeds 20% P_2O_5 (8.73% P) the name phosphate rock is used. Phosphate rock of marine origin is called phosphorite. The phosphorus content of marketable concentrates is expressed as % BPL (bone phosphate of lime) or TPL (triphosphate of lime) (1% BPL = 1% TPL = 0.458% P_2O_5 = 0.200% P).

NATURAL AVAILABILITY

The average concentration of phosphorus in the upper lithosphere has been estimated by different authors to be between 0.08 and 0.12% by weight (Table 1).

TABLE 1

Estimated average concentration (in % by weight) of phosphorus in the lithosphere

Igneous rocks	Sediments continent	Sediments oceans	Soils	Continental crust	Reference
0.13					Clarke & Washington (1922)[a]
0.076					Vogt (1931)[a]
0.118					Goldschmidt (1937)[a]
	0.058	0.118			Niggli & Niggli (1952)
0.12					Conway (1945)[a]
0.090			0.080	0.090	Green (1959)
0.093	0.077			0.093	Vinogradov (1962)
				0.120	Lee & Yao (1970)[b]
				0.100	Cathart & Gulbrandsen (1972)[b]
Averages					
0.105	0.068	0.118	0.080	0.101	

[a] See Rankama & Sahama (1949).
[b] See US Geological Survey (1973).

Geochemistry

In the rocks of the upper lithosphere, phosphorus is present only in the pentavalent state, forming part of the orthophosphate ion $[PO_4]^{3-}$. Even in low concentrations phosphorus tends to form independent minerals and more than 200 natural phosphates have been described. Their greatest variety is found in pegmatites and as alteration products in superficial deposits. Several phosphates are mined for their metal content (lithium, rare earth metals, thorium and uranium). Because of their low overall abundance, however, these minerals usually do not constitute a source for phosphorus. Most

phosphorus, possibly as much as 95% (Rankama & Sahama 1949), occurs as fluorapatite, which is a common accessory mineral in most rock types, normally in concentrations of less than 1%. It also is the major commercial phosphorus mineral.

Igneous and metamorphic rocks

The composition of apatite in igneous and metamorphic rocks is near to $Ca_5(F,Cl,OH)(PO_4)_3$, in which Cl^- and OH^- may substitute for F^-.

The P_2O_5 content of apatite ranges from 41 to 42.5% (about 18.4% P) and the fluorine content from 3 to 4%. Thus, apatite is a major fluorine mineral, binding a substantial amount (up to 35%) of the fluorine in the upper lithosphere. The specific gravity is about 3.18.

In calc-alkalic rocks phosphorus tends to be concentrated during the earliest steps of the main stage of crystallization. It is somewhat more abundant in hornblendite, gabbro and diorite than in granodiorite and granite.

In alkalic rocks such as syenite, nepheline syenite and especially in basic alkalic rocks phosphorus may become enriched to a main constituent and apatite becomes a rock-forming mineral. In the Lovozero massif (Kola Peninsula, USSR) such a residual magma, rich in phosphorus, intruded into the surrounding rock and formed vast bodies of apatite rock. These have supplied about 2/3 of the phosphate produced in the USSR. According to Emigh (1973) the recovered ore averages 7.42% P, which is upgraded to a concentrate containing as much as 17% P. In the Phalaborwa complex (South Africa) apatite, associated with serpentine–olivine–magnetite ('phoscorite'), occurs in a 120 m wide zone around a central carbonatite core. The phoscorite has an average phosphorus content of 4.3%. It transgresses into a surrounding body of pyroxenite, roughly 17 km^2 in surface area. Apatite occurs as disseminations in this pyroxenite. Sampling indicates an average P content of 2.6%. An analysis of 163 samples indicated that the concentration ranges from 0.61 to 5.19%, averaging 2.66% P. Areas with higher than average content do occur (Geological Survey of South Africa 1959). Since 1965 annual production has been in the order of 1.3×10^6 tonnes (1.3 Mt) of concentrates averaging around 15% P.

Some 200 alkalic igneous complexes associated with carbonatites are known from all over the world. Several can be mined for their phosphorus content, especially where residual concentration of apatite has occurred at the surface (e.g. in Canada [Erdosh & Sandvik 1976] and in Brazil [Cruz et al. 1976]). Currently about 17% of the world production of phosphate rock derives from igneous rocks (mostly from the Kola Peninsula).

Sedimentary rocks

During weathering, residual soils tend to become enriched first in apatite. Eventually, phosphorus will be liberated from its minerals. Through uptake by plants it enters into the biosphere. Some phosphorus is removed by weathering solutions and some is reprecipitated as calcium, iron or aluminium phosphate. The remainder is carried to the sea. Some apatite is transported mechanically to this environment. Table 2 shows average phosphorus contents for different sediments (Niggli & Niggli 1952).

TABLE 2

Estimated average concentrations (in %) of phosphorus in sediments[a]

Continental	Average (range)	Oceanic	Average
Sandstones	0.0350 (trace–0.33)	Red clay	0.1300
Shales	0.0740 (trace–0.30)	Blue mud	0.0920
Carbonates	0.0170 (trace–0.13)	Globigerina-ooze	0.0790
Averages	0.0580		0.1180
Weighted average for all sedimentary rocks			0.1030

[a] Source: Niggli & Niggli (1952).

Hydrosphere

Fresh waters commonly contain less than 5–10 mg/t (as phosphate) and, in spite of constant addition of phosphates to the sea, the concentration of phosphorus in ocean waters normally does not exceed 0.1 g/t as phosphate and 0.016 g/t organic phosphorus.

Phosphate is removed from sea water by organisms. Especially in the upper layers the phosphorus concentration is usually below average. In the cool, deeper layers, however, sea water appears to be saturated with respect to phosphorus. Excessive phosphate is precipitated (organo)chemically or removed from sea water in the skeletal structures of marine organisms. These may be rich in phosphorus, often as carbonate–hydroxyapatite (dahlite). In sea water, with time, the hydroxy group will be replaced by fluoride and the most common form of marine phosphate is as pellets and nodules of micro-crystalline carbonate–fluorapatite or collophane. Its composition is given as $Ca_{10}(PO_4)_{6-x}(CO_3F)_x(F,OH)_2$ with a value for $\bar{x}$ close to 1. Francolite and staffelite are synonyms for carbonate–fluorapatite. An important substitution

of PO_4^{3-} by SO_4^{2-}, associated with replacement of Ca^{2+} by Na^+, is sometimes observed. Many other elements may (partially) substitute for Ca^{2+}, PO_4^{3-} and F^-, a fact which explains the great number of trace elements usually found in marine apatites. Apart from fluorine, uranium, vanadium and rare earth metals eventually may constitute valuable by-products.

Marine deposits

Favourable conditions for the concentration of phosphate at the sea bottom exist in areas of upwelling deep ocean water at the edge of land masses (see, e.g. Kazakov 1937; McKelvey *et al.* 1953; Gulbrandsen 1969). Such areas are found in the trade-wind belts on the west coasts of continents and on the equatorial side of marine basins. Significant concentrations also may form where warm poleward-moving superficial currents meet cold countercurrents in a shallow water environment (30–300 m). Estuarine environments or closed basins on the continental interior sometimes may act as favourable environments for the concentration of phosphorus.

Phosphate nodules on the sea floor

Phosphate nodules and grains are found on the sea floor on continental margins, mainly on shelves but also on submerged mountains where such favourable conditions as those just described existed. They have been reported from the west coasts of the USA and South America; from the east coast of the USA and from the Argentine; from Spain; the coasts of Southwest and Northwest Africa; the Agulhas Bank; the east coasts of Japan and Australia; the Chatham Rise east of New Zealand, *etc.* Baturin & Bezrukov (1976) have dated phosphate nodules from the Peru–Chile shelf and from the Southwest African coast as being from late Pleistocene to Holocene. Other nodules apparently are relatively ancient and date from early Pleistocene back to pre-Quaternary and, in several cases, even late Cretaceous. The nodules contain from 8.7–14% P. Emigh (1972) estimates some 300×10^9 tonne (300 Gt) of such nodules on the sea floor.

On the west coast of Baja California the beach and near-beach sands over a length of 80 km contain an average of 1.5% P and higher grade sands can be found on the sea floor to the west. Until recently, phosphate nodules could not be mined competitively from the sea floor.

TABLE 3

World phosphate resources (in Mt of phosphate rock)

Country	USBM (1975)[a]		Slansky (1975)[f]	USGS (1973)[c]	USBM (1972)	USBM (1971)[e]	USBM (1965)[e]
	reserves[b]	resources	reserves (ore in place)	identified resources	reserves	indicated reserves	resources
North America							
USA	2268	6350	54 230	9750	7121	44 120	45 928
South America							
Peru	73	454		700			1425
Brazil							1900
Europe							
USSR	726	3628	11 000	25 100			24 000
Africa							
Algeria	100	136	>500				3170
Egypt	181	363	1130				630
Morocco	9071[d]	54 431	45 000		29 937	60 000	66 500
Senegal	118	181	200		32	113	126
South Africa	91	136					
Spanish Sahara	1542	3357	1600		26 762		341
Togo			100		110	340	380
Tunisia	454	1814	1200		4536	5940	6335

Asia						
China	ˋ 54	2531		3786		
Israel	36		80			
Jordan	91		>750			
North Vietnam	64					
Syria	454		830			
Oceania						
Australia	907	2722		1428		
Pacific Islands	109	136	260	46	126	
Others	138	277				25 451	30 940	2216

[a] US Bureau of Mines

[b] Estimated recoverable reserves at $27.66 per short ton. published Phosphate Rock Export Association 70 BPL Price. f.o.b. Florida plant. effective July 1,1974 and competitively marketed at this selling price.

[c] US Geological Survey.

[d] Minimum reserve. Reserve may be as large as 36 Gt.

[e] Resources given as P_2O_5 or P are recalculated to phosphate rock at 14% P.

[f] Personal communication.

Phosphorite deposits

Through geological history, the largest and richest phosphate deposits in the world appear to have formed in marginal troughs (miogeosynclines) in areas of upwelling deep ocean waters, where a lack of or slow rate of sedimentation other than apatite occurred. The deposits are characterized by a typical rock sequence of black shale, phosphatic shale, phosphorite, dolomite, chert or diatomite and saline deposits, and red or light-coloured sandstone or shale. Carbonaceous matter is a common constituent of the phosphorites and the black shales. Individual beds of phosphorite may be one or more metres thick and contain 13% or more phosphorus. They may extend over hundreds of km^2. Phosphorite that was formed on the adjacent stable shelf area is usually associated with lighter coloured rocks and the individual beds tend to be thinner. The phosphorus content may vary between 8.73 and 13% P.

The Permian Phosphoria formation of the western USA may serve as a prototype for phosphorite deposits that were formed this way. The main bed is 1.5 m thick and averages close to 14% P. Other, lower grade, beds with a combined thickness of 23 m contain between 6 and 10% P.

McKelvey *et al.* (1953) estimated the original area of phosphate deposition at some 3.5×10^5 km^2 and the total phosphorus deposited at 700 Gt. Cathart & Gulbrandsen (US Geological Survey, 1973) quote against identified resources of 0.78 Gt P in rock averaging 13% P a total current resource potential of 16 Gt P of which 7 Gt is in rocks containing more than 10.5% P.

Other examples are found in Morocco (Khouribga, Yousoufia, Ben Guerir). In a rectangular area of 50×200 km south of Casablanca and east of Safi, phosphorite occurs in flat-lying beds from 1 to 9 m thick (average 2 m) and contains 14–16.4% P. The age of the deposits is late Cretaceous to Eocene and reserves of 40 Gt of phosphate rock are quoted by Emigh (1973). The phosphorite deposits of Spanish Sahara, which in 1976 was turned over by the Spanish government to Morocco, are of similar type. Reserves are quoted as 1.7 Gt of ore in a 3.6 m thick bed averaging some 14% P. In Algeria and Tunisia similar deposits with average P content of 12.4% are found in from one to three beds which may be up to 4.5 m thick. Other deposits are found in Egypt, Syria, Jordan and Israel. Together they form the Tethys or Mediterranean phosphogene province of late Cretaceous-Eocene age (Sheldon 1964), which is at least as large as the Phosphoria Province of the USA and Canada. The large deposits of Kara Tau (USSR) and Chubsugul (Mongolia), the Cambrian deposits of the Georgina Basin (Australia), the Miocene deposits of the Sechura Desert in Peru as well as the Cretaceous deposits of Colombia all

have been considered to have a similar origin. Together, phosphorite deposits constitute over 80% of the conventionally estimated potential reserves (Table 4) and have supplied nearly 80% of the phosphate rocks produced.

Phosphatic marls and limestones

These are sedimentary beds with significantly higher than average phosphorus content but less than in phosphorites. They may form when phosphate is deposited alternating with carbonate rock and/or together with other detrital materials. They are usually too low-grade for treatment but the crude material can be used locally as fertilizer. Such beds may form the source for secondary concentrations.

Secondary concentrations and enrichment

The phosphate deposits of Florida (USA) are an example of secondary concentration from phosphatic limestone.

Land pebble phosphate occurs in the Pliocene Bone Valley formation over a roughly circular area of 6400 km^2. The ore (or matrix) is a gravel consisting of 10–50% phosphate pebbles in a matrix of sand, clay and soft phosphate, along with fossil teeth and bones of land and marine animals. The pebbles are derived from the disintegrating and sorting effect of ocean waves on underlying coastal phosphatic beds, mainly of the Miocene Hawthorne formation, and the subsequent submarine reworking of the phosphate-rich residuum. The nearly horizontal beds are from 0 to 15 m thick (average 4.9 m). In the mine area the ore contains 3–4.5% P which is upgraded to a product containing some 14.5% P. Phosphorus recovery from the ore is about 67%.

River pebble occurs as bars and banks in stream channels and consists of pieces of phosphate concentrated by the streams where they have crossed underlying phosphatic beds.

Hard rock deposits are residual accumulations with successive deposition and redeposition of phosphate dissolved from overlying beds and deposited in underlying calcareous beds by replacement and cavity filling.

Brown rock deposits (Tennessee) are of similar origin and are derived from Ordovician phosphatic limestone. Their phosphorus content in place is between 8 and 11.5% and they can be easily upgraded to some 16.6% P.

The Florida deposits have supplied more than 500 Mt of phosphate rock (76% of USA production since 1870), mostly land pebble.

Guano and deposits derived from guano

All large accumulations of guano are formed at the land surface by sea birds. Smaller quantities are formed in caves, principally by bats. The mineralogy of guano deposits is complex.

When soluble phosphate is carried downward to underlying limestone, apatite is formed and replaces the limestone. If the underlying rock is of volcanic origin, aluminium or aluminium–iron phosphates are formed. Guano or deposits derived from guano are the earliest sources of phosphate fertilizer. They still account for over 4% of world phosphate production, mostly from the western Pacific. Individual reserves are measured in 10^6 t and their phosphorus content may be as high as 16–18%.

Resources and potential reserves

From the foregoing description of phosphorus deposits in the upper lithosphere, total resources for a resource base consisting of the dry land surface of the earth (1.5×10^8 km^2) to a mineable depth of 2.5 km can be estimated at some 10^{18} t of rock containing 0.1% P or roughly 10^{15} t of phosphorus. These resources are distributed over individual deposits containing several gigatonnes (Gt) of rock each, with average phosphorus concentrations ranging from less than 0.1% to over 13%. The theoretical maximum concentration of 18.4% P in fluorapatite sometimes is approached in much smaller deposits of nearly pure apatite rock. Table 3 gives different estimates of phosphate resources of possible economic interest, expressed as Mt of phosphate rock, for this environment. The estimates vary between 44 and 140 Gt of phosphate rock, which at an average grade of 14% P would contain from 6 to 20 Gt of phosphorus. They are divided between some 30 different countries. Morocco (32–72%), USA (8–46%) and the USSR (5–16%) between them control 85–94%.

Such potential reserves, expressed as a fraction of 6–23×10^{-6} of total resources of the environment, are extremely large with respect to the comparable average of 3.3×10^{-6} for 18 metallic and non-metallic mining products of similar economic importance—ranging from 4.1×10^{-8} for aluminium to 8.9×10^{-6} for gold (Brinck 1976a). The sea floor, which through geological history always seems to have been a particularly favourable environment for the concentration of phosphorus, adds another 300 Gt of phosphate nodules (> 26 Gt P) to the resource base. A relatively important fraction of these additional resources may prove recoverable in the future at competitive prices.

PRODUCTION

The first phosphate-fertilizer materials used were animal manure, bones, fish, guano and marl. Some uses date back to antiquity and these resources were usually renewed almost as fast as they were used. This renewal of phosphate resources is a continuous process and sometimes poses severe pollution problems. For the purpose of this paper I shall not consider the recycling of phosphorus.

Mining of phosphate rock started in 1845 in Spain and soon after in France and England. Peruvian guano, however, had been imported into England since 1820 and by 1861 imports had totalled 3.2 Mt, indicating an average annual world production of at least 80 000 t around the middle of the 19th century (Blakey 1973). Phosphate mining started in the USA in 1867 with a few t of Carolina phosphate rock but by 1870 production had already reached 66 000 t. Table 4 shows the development of world production since 1940 when some 12 Mt of phosphate rock were produced. From statistics on production in the USA it can be seen that, after an initial rapid growth (8.64%) until 1920, a relatively stable level of production was maintained until the end of World War II. After 1945 world production increased to 106 Mt in 1976—an eight-fold increase in about 30 years or an average annual growth close to 7%.

Production in the USA until 1977 adds up to some 900 Mt and world production is estimated at over 2.2 Gt containing an estimated 300 Mt of phosphorus.

Expressed as a fraction of total resources (1.5×10^{-8}) the annual phosphorus production of 15 Mt P contained is small with respect to the comparable average of 7.37×10^{-8} in 1970/71 for 18 mineral commodities of comparable economic importance (e.g. 1.84×10^{-10} for aluminium and 4.14×10^{-7} for gold).

PRICE

A period of relatively stable prices with increasing production during the period 1954/68 was followed by overproduction and deteriorating prices which in 1972 went down as low as $5.62/t of 13.6% P rock in the USA. This fall followed a period of rapid growth which from 1964 to 1968 averaged 10.4%. In 1973 apparent demand exceeded production and prices improved (see Table 5).

The average value at the mine for phosphate rock in the USA during the period 1954–1973 was $6.49/t or US¢ 4.78/kg P contained. The world average for 14.2% P (70–72% TPL) rock can be estimated at $7.20/t or US¢ 5.07/kg P.

TABLE 4

Phosphate rock production, major producers and prices

Period	Annual production (in Mt)	Growth rate (%)	Price ($/t)^a	Production (%) by country				by type		
				USA	USSR	Morocco	Tunisia	sedimentary	apatite	guano
1940	12.0			33	8.5	13	16	74	10	16
1954/58	32.7	6.46	6.19	44	17	16	6	81	12	7
1959/63	45.0	6.59	6.70	41	19	18	5	78	15	7
1963/68	71.6	9.73	7.13	45	21	14	4	77	18	5
1969/73	87.8	4.16	5.92	41	22	15	4	79	17	4
1974	109.0	5.81^b	12.10	13.57%	15.05%	14.44%	12.70%			
1975	106.0	4.44^b						P contained (1973)		
1976	106.0	4.78^b								

^a Value of USA marketable rock production at the mine; comparable world average is estimated US $7.20/t (14.2% P) or US $0.0507/kg P contained. Average value at mine of US phosphate rock for 1954/73 was $6.49/t or $0.0478/kg P contained.
^b 5-year averages.

TABLE 5

Listed exporters' prices for phosphate rock for the period 1971 to 1976

Exporting country	Quality (% TPL)	Price (US $/t)							
		1971	1972	1973	Jan. 1974	July 1974	Jan. 1975	Jan. 1976	Jan. 1977
USA	75	10.0	11.0	12.9	27.1	41.3	55	35–40	31
	70–72	8.9	9.9	11.3	23.6	35.4	48	30–35	26.75–28.50
Morocco	75	11.75	11.75	14.2	42	63	68		
	70–72	10.15	10.15	13	40	60	65		38
USSR							50		

Production costs for marketable rock in the USA range from $4.4 to $8.8/t (US Bureau of Mines 1975). Cost-related prices were expected to increase to a little over $7.00/t for US rock by the year 2000 (US Bureau of Mines 1972).

In November 1973 the major phosphate-exporting country, Morocco, raised the listed export price for 15% P rock (75% TPL) from $14.2/t to $42.0/t. This overnight increase in price of 200% followed similar earlier price developments in the gold and petroleum industries. Such listed prices are used as a basis for negotiation and do not represent actual selling prices. According to Freeman (1977), however, during 1974, when production reached a maximum of 109 Mt rock (see Table 4), contracts were concluded at prices ranging between $35/t and $100/t.

Apparent demand of 113 Mt in 1974 slumped to 103 Mt in 1975 and 104 Mt in 1976. Prices, which had been maintained during 1975 went down by $18–20/t in 1976 and US triple superphosphate and diammonium phosphate sold more cheaply in Europe than the published export price (free on board, at Tampa) for the rock used for their production.

In December 1976 in Paris, Morocco, Tunisia, Senegal and Jordan established 1977 prices with Khouribga 14.4% P (72% TPL) rock (free alongside ship at Casablanca) at $38.0 as a standard reference. Phosrock (Florida) quotes $28.50 to European customers for similar grade material and other producers are some $5.0 below this price.

With the current prices, assuming either an infinite elasticity of demand or an effective mechanism to keep world production in line with apparent demand at these prices, almost all previously estimated potential reserves could be considered exploitable at costs below market price. The fact that this is not usually done (Table 3; US Bureau of Mines 1975) shows that price alone, when not closely related to production costs, cannot be used as a criterion for the exploitability of mineral deposits, whether we want to call them reserves (in the miner's sense) or just 'exploitable' resources.

RESOURCE APPRAISAL

Economic geology and metallogenetic theory are indispensable tools for the discovery, description and interpretation of specific mineral deposits, often of great economic importance. For a quantitative appraisal of mineral resources we have to use the geostatistical theories and methods that have been developed for the estimation of the reserve potential of individual mines, ore deposits or mineral prospects, by extending the concept of 'prospect' to a resource base comprising the total dry land surface of the earth to its mineable depth (here taken as 2.5 km). The grade and size distribution of individual

deposits for any element can be inferred with a log-binomial frequency function from the element's average concentration and dispersion in this environment (Brinck 1976a,b). A dispersion coefficient determines the standard deviation of the distribution for any subdivision of the environment and thus the probability for an element to become enriched in mineral deposits (resources) of any given size/grade specification. The dispersion coefficient, representing an absolute measure of the tendency of an element to become concentrated in mineral deposits, is typical for each element in a given environment and therefore has been named the specific mineralizability (Q) of an element for that environment. Using the size of demonstrated ore reserves, divided by the size of the resource base, as the measured frequency of occurrence of ore deposits of given average grade and size, the specific mineralizability as well as the resources for all possible size/grade specifications can be inferred by interpolation or extrapolation.

Until 1971, the average concentration and specific mineralizability to a large extent determined the long-term differences in price between the mining products of different elements. Thus, 'target prices' could be established for many industrial elements which reflected their long-term average prices with a probable error of 13.7%. In the absence, since 1971, of a generally accepted international monetary standard, these target prices constitute a valid set of references for our concept of 'value' which, we hope, does not change as fast as the rates for currency exchange or the prices of mineral products.

Defining a 'statistical price unit' (SPU) of an element as its target price, we could define exploitable resources as all mineral concentrations (ore deposits) of an element that can be exploited at costs up to this statistical price unit.

MIMIC (Mining Industry Model for the Inventorization and Cost evaluation of mineral resources; Brinck 1971) is an econometric model which was developed by the Commission of the European Communities to estimate world resources of uranium in different cost categories. Average production costs are calculated by a Discounted Cash Flow method as a function of the size and grade of individual deposits and the chance of finding them in the geological environment. For technical or economic reasons (or both) several restrictions and conditions were stated for the resource and cost estimates:

(i) the highest possible concentration of an element is determined by the concentration in its most common ore mineral;

(ii) costs are corrected for the specific gravity of the ore;

(iii) scale economies are possible on the production costs for daily ore-handling capacities up to 250 000 t and on the capital investment costs for daily ore-handling capacities up to 32 000 t;

(iv) for deposits with annual capability exceeding 10% of world require-

ments, costs are calculated as for deposits producing 10% of these require-
ments. Excessive ore, after amortization of investments, is valued at dis-
counted unit-exploration cost.

By eliminating restriction (iv) we can infer exploitable resources directly as
a function of the average concentration and specific mineralizability. The
applicability of the model can be extended to mineral resources of other
mineral commodities when the indicated ore grade is well below the barrier
grade (i) for the elements in question.

Phosphorus, with a barrier grade of 18.4% P and ore deposits in the range
from 4.3 to > 16% P, appears to be a marginal case. For phosphorus, a value
of 0.1975 was found for the specific mineralizability on the assumption that at
least one deposit exists with an average grade of 14% P and containing 780 Mt
of phosphorus (indicated reserves of the Phosphoria Formation—Bateman
1949; US Geological Survey 1973). The corresponding target price is US
\$0.0509/kg P which is close to the long-range average price of US \$0.0507/kg
P for the period 1954–1973. For this value of the specific mineralizability and
average concentration of phosphorus in the earth's upper crust, the inferred
exploitable resources amount to some 42 Gt of contained phosphorus, with
restriction (iv) invalidated.

A conservative assumption that, of the 6 Gt phosphorus in identified
resources (US Geological Survey 1973), at least 3 Gt occur in ore deposits with
an average grade of 13% P and containing 200 or more Mt of phosphorus each,
gives a specific mineralizability of 0.193, a target price of US \$0.0564/kg P and
inferred exploitable resources well over 40 Gt P. Calculated with the MIMIC
model, however, the inferred exploitable resources are substantially larger.
For a standard depletion time of 16 yr and annual production capacity of 10%
of 1976 production, the optimum deposit size is 24 Mt of contained
phosphorus. Fig. 2 shows the production costs for such deposits as a function
of grade. Minimum production costs of \$0.0458/kg P were found for ore
deposits with an average grade of about 14% P (when exploration costs are
taken into account). Allowing for a 15% implicit profit (royalties *etc.*) as an
industrial average, the target price (SPU) should be about \$0.0527/kg P
(\$7.60/t 70–72% BPL). According to the definition of exploitable resources,
all deposits of this size with an average grade of 10.6% P or more can be
considered as inferred exploitable resources. According to the model, they
can be estimated at 100 Gt of phosphorus. The difference from the 40 Gt
estimate is explained by the overflow conditions which occur when the log-
binomial enrichment exceeds the barrier grade. It often has been observed in
geochemical studies and during the valuation of mineral deposits that con-
centrations near the barrier grade show a higher frequency of occurrence than
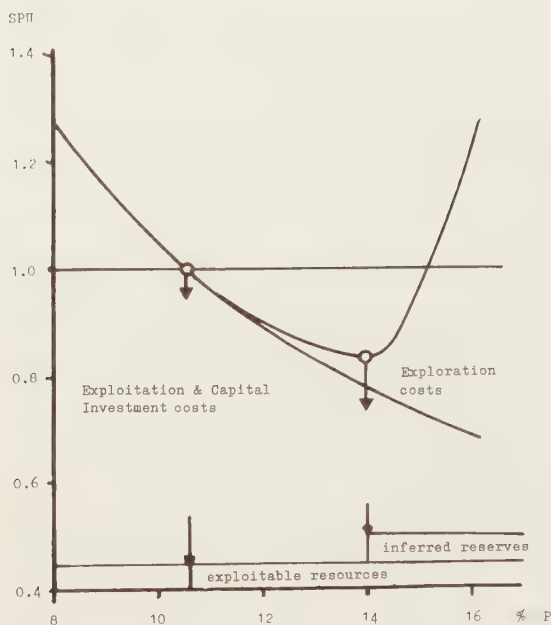
FIG. 2   Production costs (as a function of grade, in % P) for deposits containing 24 Mt P each: SPU, statistical price unit (see p. 38).

predicted from the log-binomial (log-normal) distribution of their grade variable. The barrier grade itself, however, is reached seldom and never in deposits of the size indicated from the specific mineralizability and average concentration. De Wijs (1976), therefore, has proposed the substitution of the logarithmic transformation of the grade variable $z = \ln x$ by the universal grade transformation $z' = \ln[bx/(b-x)]$ where $0 \rightarrow x \rightarrow b$ and b is the barrier grade.

Optionally incorporated in an advanced version of the MIMIC model (International Resources Consultants 1975) the consequences of this proposal have been tested. The new estimate, based again on the Phosphoria reserve estimate, indicates a specific mineralizability of 0.261. Except for the degree of enrichment of phosphorus in its ore deposits, which is depressed by the barrier grade, most observations seem to support this higher value for the specific mineralizability. In particular the occurrence of major phosphorus reserves in only a few phosphogene provinces is typical for elements with Q values greater than 0.25, such as Cr, Pb, Sn, W, Mo, Sb, Hg and Au.

The lower-than-normal ore-grade enrichment for this value of the specific mineralizability invalidates the empirical relation between average concen-

tration, specific mineralizability and price. With a target price of $0.0527/kg P as the statistical price unit, the cost figures of Fig. 2 are still valid. Inferred reserves at minimum production costs of 0.85 SPU for ore deposits with an average grade of about 14% phosphorus amount to 21.5 Gt of phosphorus contained. Exploitable resources in deposits with an average grade of 10.6% P or more can be inferred as 500 Gt phosphorus contained.

The inferred reserves of an element can be estimated independently from the size and growth rate of annual production. For the historical growth rate of 6.91% for the period 1956–1970/71 and annual production of 11.3 Mt P, some 20 Gt of inferred phosphorus reserves can be estimated, to which should be added the previous production of some 300 Mt P to make the estimate comparable with the MIMIC estimates.

The higher value of Q, in line with the geochemical behaviour of phosphorus in the environment and the rather unexpected recurrence of inferred reserves of some 20 Gt P in deposits near the average grade and production costs until 1973, seems to make the new estimate shown in Fig. 3 superior to estimates based on the log-binomial distribution of the grade variable alone (indicated by dashed lines in Fig. 3).
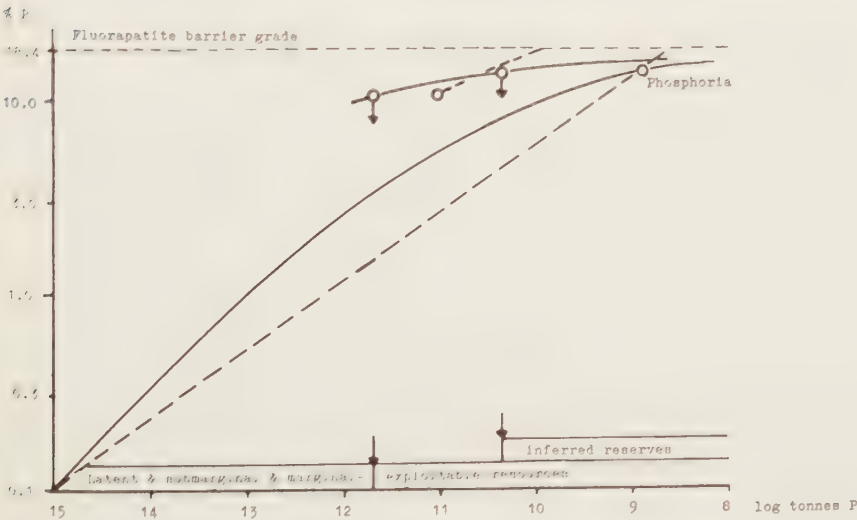
FIG. 3 New estimates of inferred reserves of phosphorus by MIMIC (IRC/76/06/P), with a higher value of Q (0.26138) and the universal grade transformation with $c = 0.001$ and R, the resource base (see p. 24), $= 1.0 \times 10^{18}$ t.

OUTLOOK

Based on the different resource estimates, the major question seems to be whether the 500 Gt P in inferred potential reserves can be produced at constant costs (according to our 1973-value definition) or will become twice as expensive (scarce) during the period of their depletion. In view of price developments since 1973 this question may seem trivial. Actually it is not. The answer determines how the natural availability of phosphorus contributes to the growth potential of our civilization.

In a simplified way, Gabor & Colombo (1976) stated the problem as follows: phosphate production, of which 80% is used for the manufacture of the fertilizers needed to feed a growing world population, historically has shown an average growth rate of 6.7% or 2.7-times the rate of population growth. Question: When will the population outgrow the production capabilities of the phosphate deposits required to feed it at the current *per capita* level?

Any specific answer to this question, scientifically speaking, should be given zero probability to be correct. Economically, however, when formulated with the assumption of current technology and all other factors remaining unchanged, such answers do not necessarily have to be meaningless.

The observed relation between the growth rate of annual production and the size of inferred reserves, which seldom exceeds the size of the exploitable resources as inferred by MIMIC, may be helpful in this respect.

The 20 Gt of phosphorus reserves inferred from the growth rate of annual production are substantially less than the 40–500 Gt phosphorus in exploitable resources inferred by MIMIC. Therefore, at present, population growth seems not to be regulated by the production capabilities of phosphorus deposits.

For 500 Gt phosphorus in exploitable resources, the relation indicates nearly 47 yr of continued growth at 6.7% before the inferred reserves from growth would equal this amount; for 40 Gt this point would be reached after only 8 yr. Thereafter, to maintain the growth rate, production costs would have to increase at an average of 0.6% annually. With other factors remaining unchanged, however, that means that we may continue to count on human ingenuity, which historically has managed to lower production costs at an annual rate of between 0.5 and 1.0% (Mabile 1968). Thus, allowing for a precarious balance between supply and demand, growth of production at the current rate probably could be maintained almost indefinitely.

As an economic geologist and wanting to be on the safe side in my estimates, the major requirement for an ample and continuous supply of

phosphorus appears to me to be that humanity continues to think about these problems and to use its ingenuity to solve them.

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Discussion

Nicol: Dr Brinck, is there any estimate of the degree to which phosphorus has been dissipated over the surface of the earth? Can the loop be closed so that we don't need to rely on the mined rock?

Brinck: I was talking about the earth's continental crust. Soils appear to be slightly depleted in phosphorus with respect to the crust's average (see Table 1 in my paper). Most of the phosphorus passes through the ocean where it is precipitated in the form of phosphate nodules. There are at least 300 Gt of nodules on the sea floor. That means 30 Gt of phosphorus (see p. 29). They have been dated as being from late Cretaceous to recent times and their recycling to the crust and soils should be measured in many million years.

R. J. P. Williams: Would you count phosphate nodules as a non-exploitable source since they are so dispersed?

Brinck: No; they are not exploited now but certainly are a potential reserve. If we developed the technology, we could mine them like manganese nodules.

Kabbaj: Is the figure of 20 Gt for the inferred reserves of phosphorus (p. 41) derived from your model and, in particular, based on a depth limit of 2.5 km? If so, can the model show how big the reserves would be if we consider a depth of 100 m, which is three times the present highest average figure for mining depth?

Brinck: Those reserves inferred from the growth rate correspond to the 20 Gt of demonstrated reserves as estimated by the US Bureau of Mines and the US Geological Survey on several occasions and also by the Bureau de Recherches Géologiques et Minières in France. Some people prefer to call

them demonstrated resources because reserves, by definition, could never contain much more than currently-producing deposits plus the amounts needed for the installation of new production capacities to meet the growing demand. Thus, reserves always tend to be proportional to the requirements at a given time and seldom exceed 15–20 years' production at the current growth rate (68 years for phosphorus). The exploitable resources predicted by MIMIC (40–500 Gt P) are to be found in the environment to a depth of 2.5 km. Other minerals are mined to this depth at comparable prices. (The cost that counts is the cost of producing a marketable product from the ore, i.e. it is independent of the element contained in the ore.) When the element concentration in the ore is high, unit cost for the element will be low and *vice versa*. Thus, producing gold from a 15 g/t gold ore at 2.5 km depth is almost directly comparable to producing a 72% BPL (14.2% P) concentrate from phosphorites occurring at the surface. However, common sense demands that one would not consider working a deposit of given grade and size at 100 m depth if one could mine a similar deposit at the surface—why mine high-cost ore when one can mine low-cost ones, even if the distinction between the two could be as little as 1 US cent/t of ore mined? This is a problem the economic geologist will always face.

Pirie: I gather that your model concerns itself with phosphate—that is, phosphorus that has been through the biological cycle. Are there any non-biological phosphorus ores? Is phosphorus ever concentrated in a non-biological way?

Brinck: About 80% of present production comes from phosphorite and about 17% from igneous rocks (mostly from the Kola peninsula, USSR) where it occurs as nearly pure apatite intrusions (see p. 27).

Pirie: Does phosphorus always occur as phosphate?

Brinck: Yes. Many different phosphates are known but the only commercial phosphate mineral is apatite. The average grade of igneous apatite ores is usually less than in phosphorites which average over 13% P. In igneous rocks apatite may occur in small rich deposits (nearly 18.4% P) but these usually cannot be mined separately. Mined as a mass, the ore contains about 8% P. In South Africa the average is not more than 4.6%.

Griffith: There are no deposits of phosphorus on earth other than phosphates. If phosphite or phosphorus in a lower oxidation state is found, the material must be a meteor, not a natural deposit.

Pirie: In what form would it be in a meteor?

Griffith: A metal phosphide.

Pirie: Deeper in the earth would one find phosphides?

R. J. P. Williams: If there were any phosphorus in the iron core it would be in the reduced form.

Tinker: Dr Brinck, has your model been validated?

Brinck: No, but there is so much coincidence—especially the observed relation between long-range price, specific mineralizability and average concentration for many different mineral commodities—that it must be valid. And these parameters are verifiable.

Tinker: Are there not large fields of probability generated by the model in which the data could be anywhere and still fit the model?

Brinck: Yes; the variation in costs between similar deposits could be enormous but most of them still would fall well within the economic ranges. The model calculates average prices; of course, there are deposits that can be worked easily, at well below average prices, and those that cannot be worked at average prices.

Tinker: The model, if I understood it correctly, is based on the assumption that the specific mineralizability Q is constant at each step in the concentration sequence. Is that likely?

Brinck: No; but it does not matter too much as long as the deviations from the average are not systematic. In another model we found that over eight subdivisions in nearly all cases (I say nearly because this is a probabilistic theory) one can take an average Q value as long as the concentration does not go too close to the barrier grade. This was the challenge with phosphorus; the ore grades are close to the barrier grade. That is why I also used the universal grade transformation, which has not been tried before for this purpose. But even if one does not use it, there still is this enormous resource of 500 Gt P in potential reserves which could be exploited at costs less than twice the current long-term average price.

Tinker: Isn't the sort of cascade process you postulate particularly unlike the biological concentration processes?

Brinck: As a non-biologist it does not seem likely to me. Are similar cascade processes seen in biology?

Tinker: It is difficult to think of one. It is as if a sea-bird were to eat some other sea-bird's effluent and concentrate the phosphorus in it, and for this process to be repeated several times.

Kabbaj: I should like to link this paper with Dr van Wazer's. According to Dr Brinck, the number of times that production could be doubled before depletion of resources is roughly the same as the figure for the rate of growth. At an annual rate of growth of 7% we can double production (consumption) seven times. At that rate, production doubles every 10 years, and, therefore, we can continue for only 70 more years before depletion. In other words, according to your estimates, the increase in production that supports the increase in population cannot be maintained after the next 70 year period.

Brinck: In their report to the Club of Rome Gabor & Colombo (1976) stated that phosphate production historically increased at 6.7%, 2.7 times as fast as population growth. The observed fact that the growth rate of annual production is regulated by the size of the remaining inferred reserves predicts, on the basis of the low estimate of 40 Gt P, that we shall be in trouble within eight years but only after 47 years on the basis of the high estimate of 500 Gt. Extrapolation shows that this has been the case for the last 5000 years because, given current technology and prices, Doomsday is always just over the horizon of human knowledge. Therefore, the only way to survive is to increase knowledge. It is conceivable in this context, that we may urgently need the additional intelligence of the 200 000 people born each day (see p. 7) in order to do so and feed them at the same time, too.

Tinker: Projections for consumption of phosphorus and population growth rates are fundamental to any consideration about how resources relate to needs, but I question the assumptions on which these figures are based. They seem to be based on the idea that there is some obvious link between either population growth and phosphorus requirement, or future production of food and phosphorus requirement. Is that true? In countries such as the UK with a developed agriculture the use of phosphorus and fertilizers has not grown for several years. The market has remained more or less static, even while the rate of food production climbed rapidly. This rapid increase in the rate of use of phosphate seems to be in part a consequence of the necessity for many soils in the world to go through a stage of phosphorus accumulation: highly developed agricultural areas have already passed this stage. This rapid rate of increase cannot be regarded as normal in the long-term.

Arthur: The use of fertilizer phosphorus in the UK fell temporarily in the 1973–74 period and is now recovering, but interpretation of that fact in isolation in relation to food production is dangerous unless one has information about what is happening in the soil. Is the total amount of phosphate in the soil constant or is it falling?

Tinker: I am suggesting that there is not necessarily a linear relationship between food production and use of phosphorus fertilizers. Some of the new varieties of cereals are raised with almost the same amount of phosphorus fertilizer as before but produce much more grain than varieties in use some years ago.

Brinck: My figures are taken from the Club of Rome's working group (Gabor & Colombo 1976). For the past 25 years the growth rate for the use of phosphorus has averaged 6.7%. However, Gabor & Colombo did not claim that it was necessary to continue in this way. According to figures for reserves from MIMIC (and on the assumption that all other factors remain the same),

growth of production at the current rate could be maintained almost indefinitely (see p. 42). However, things probably will not remain the same.

Loughman: In intensive conditions such as those in the UK some agricultural crops hardly respond to added phosphate. What would be the effect of a five-year moratorium on the application of phosphate fertilizer (apart from the effect on the companies)?

Larsen: Very little in countries with intensive agriculture. Curiously, during the Second World War in Denmark when no phosphates could be bought for five years the crop yield actually increased. Most soils have a tremendous buffer capacity with regard to phosphate.

Tinker: To qualify that statement I should add that most of the British recommendations for fertilizers are based on field experiments which indicate that, on average, addition of just a little phosphorus fertilizer still raises the yield slightly. If no phosphate fertilizer were used, there would be a small drop in yield which might become progressively greater.

Larsen: Addition of phosphate at the beginning of the growing season gives the crops a good start. In some field experiments the responses to phosphate are the same as they were 70 years ago (Larsen 1976).

Kabbaj: Improved yields usually mean that the plants have to take up more nutrients supplied by fertilizers out of the soil but are there improved varieties that produce high yields with a lower demand for phosphate?

Tinker: In general, as Professor Larsen has said, more fertilizer phosphate is added than is taken up by the crop. Improved varieties of cereals, with higher yields, have not needed an equivalent increase in phosphorus fertilizer, although often the nitrogen requirement may increase. So in effect the phosphorus is being used more efficiently.

J. H. Williams: The build-up of soil reserves has meant that cereals now seldom show a direct response to phosphorus and that fertilizer phosphorus is only needed to maintain soil reserves. Maintenance dressings are related to yield; when yields of wheat exceed 5 t/ha an additional 20 kg P_2O_5/ha (8.7 kg P/ha) is recommended.

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Some economic and technical factors affecting use of phosphate raw materials

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Abstract In comparison with phosphate resources most of the other industrial minerals essential to man have much higher unit values. Furthermore, they generally have more narrowly defined geochemical origins, concentration requirements, and end-use markets. Consequently, an economic assessment of their mined production cost in relation to market value is more easily and reliably defined.

Thus, the mere knowledge of existing or newly discovered ore bodies provides economic incentives for exploitation plans --even in the most remote geographical location (as is well illustrated by iron, copper, tin, lead, and similar mineral commodities). Unfortunately, this is not the case for phosphate resources. Much of the known vast reserves of more than 1×10^{11} tons, which are favourably dispersed among the worldwide markets, remains uneconomical to recover, despite the growing need for phosphate in world food production.

A complex set of interrelated technical and economic factors decide the economic potential of any particular phosphate reserve. Although technical similarities may exist among depostis, economic analogies are rare.

The economic evaluation of the mineability of the ore and the mill preparation of the concentrates must also take into account the geological setting and character of the ore deposit as well as the eventual end-use markets and their locations.

THE PHOSPHATE ROCK INDUSTRY

The commercial production and use of phosphate rock began in the 19th century. The first recorded statistical data was for 1847 when 500 tons were mined in Suffolk, England (Gray 1944), although it is likely that there was some commercial production earlier. World production increased rapidly to 5000 tons* in 1850, 10 000 tons in 1853, over 100 000 tons in 1865, over 1 000 000 tons in 1885, over 10 000 000 tons in 1928; and over 100 000 000 tons

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* Footnote, see p. 50

in 1974. Based on projected fertilizer consumption allowances for other uses, annual phosphate rock production will probably be of the order of magnitude of 300 million tons by the year 2000 (UNIDO 1976).

Although phosphate rock has many uses, probably as much as 85% of the world's production is used for the manufacture of fertilizers (including direct application to the soil). The grade of commercial phosphate rock may be expressed as its P_2O_5 content*; the usual range is 28–38% P_2O_5. In recent years the world average has ranged from 31.8 to 32.5% P_2O_5 for 'marketable' phosphate rock sold or used by the producer.

The grade is also commonly expressed in terms of tricalcium phosphate, $Ca_3(PO_4)_2$, known in the trade as 'bone phosphate of lime' (BPL).* This term originated when tricalcium phosphate was thought to be the main constituent of bone and phosphate rock. It is now known that the phosphatic component of both bone and most phosphate rock consists of apatitic compounds.

'Commercial' phosphate rock usually refers to any rock containing a high percentage of phosphate minerals that can be used for commercial purposes such as fertilizer manufacture, direct application to the soil, or manufacture of industrial phosphorus compounds. The term usually applies to a product obtained by mining and beneficiation although in some cases the rock as mined can be used without beneficiation.

Phosphate rocks may also be classified according to their origin as sedimentary, metamorphic or igneous. About 85% of the phosphate rock used commercially is sedimentary; the remainder is mainly igneous.

Apatitic phosphates

Most commercial phosphate rocks contain fluorapatite, $Ca_{10}F_2(PO_4)_6$ as the primary, and usually the only, source of phosphorus. However, pure fluorapatite is relatively rare. The apatite structure is amenable to many substitutions, of which the most common are Mg, Sr and Na for Ca, OH and Cl for F, As and V for P, and $CO_3 + F$ for PO_4.

Most of the sedimentary rocks fall into the group called francolite or carbonate apatites. The general empirical formula for the francolite group is, as reported by McClellan & Lehr (1969):

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{0.4x}F_2$$

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* Conversion factors: 1 ton = 1.016 tonne; for P_2O_5, BPL and elemental phosphorus: P_2O_5 = 0.4576 × BPL; BPL = 2.1852 × P_2O_5; P = 0.4364 × P_2O_5; P = 0.1997 × BPL.

As x, the extent of carbonate substitution, increases, the reactivity increases. The value of x may range from nearly zero up to about 1.2 in commercial phosphate rock. The P_2O_5 content of pure fluorapatite is 42.2% (18.4% P); the P_2O_5 content of the carbonate apatites decreases with increasing carbonate substitution to a minimum of about 34% in the most highly substituted apatites.

Several phosphate rocks show substantial substitution of hydroxy for fluoride ions; these include phosphates from Nauru, Christmas Island, and Curaçao Island and the Brazilian igneous apatites. Some of these phosphates also have substantial carbonate substitution. An extreme example is Curaçao Island phosphate. It contains only about 20% of the stoichiometric amount of fluorine in fluorapatite. Presumably substitution by OH accounts for most of the remaining 30%. It also has a substantial degree of substitution of carbonate for phosphate. The island phosphates are presumably formed by reaction of coral limestone with phosphate leached from guano deposits. (They are included with sedimentary ores for convenience.)

Many igneous apatites are deficient in fluorine; some samples contain only one-third to two-thirds of the stoichiometric quantity.

Aluminous phosphates

Deposits in which the principal phosphate minerals are aluminous are fairly widespread. The deposits in Thies in Senegal and C-grade ore in Christmas Island are being mined and used. The C-grade ore is only little used at present but, as it occurs in a stratum overlying the apatitic ore, most of it is mined and stockpiled awaiting the development of a suitable economic process for its use while the apatitic ore is being marketed. A similar situation exists in Florida where a 'leached zone' containing aluminium phosphates overlays the pebble phosphate matrix. Because the leached zone is low grade and variable in composition, no attempt has been made to stockpile it.

The principal aluminium phosphate minerals are crandallite, millisite and wavellite. The chemical composition of these minerals is somewhat variable, but the following formulae are typical:

Crandallite	$CaAl_3(PO_4)_2(OH)_5.H_2O$
Millisite	$(Na,K)CaAl_6(PO_4)_4(OH)_9.3H_2O$
Wavellite	$Al_3(PO_4)_3.5H_2O$

As in apatites, various substitutions are possible; Fe for Al is a common one.

The aluminous phosphate ores contribute only a small percentage to present world use. However, they can be used for fertilizer manufacture by a

nitrophosphate technique or, in some cases, for direct application after calcining. Aluminium phosphate minerals also occur as accessory minerals in some apatitic deposits.

Accessory minerals

Phosphate deposits contain a wide variety of accessory minerals; the value of the deposit often is related to the amount and character of the accessory minerals and the ease or difficulty of separating them from the phosphate. Perhaps the most common are silica, which may be present as quartz or in hydrous forms such as chert, clays, and other silicate minerals such as feldspar, mica, *etc.*, and carbonates, mainly calcite and dolomite.

FACTORS AFFECTING MINEABILITY

To define the mineability of a low-value mineral such as phosphate we must consider technical and economic factors at the same time. The difficulty in making a practical assessment of mineability is that no one factor is absolute. For each deposit there exists a unique combination that defines whether mining is both technically and economically feasible. Phosphate deposits differ so much in their geological character that precisely parallel conditions rarely, if ever, exist.

From the case histories of successful mine operations, however, it is possible to establish some limits on the flexibility of factors that allow economic mining in current conditions. At present, this usually requires high-volume removal of waste overburden plus ore, large annual tonnage output, high recovery efficiency, and upgrading to prevailing market-grade specifications. Some deposits need little or no removal of overburden or beneficiation. Such favourable conditions can make small tonnage output profitable, especially if cheap labour is abundant.

The basis for making the assessment of mineability can change rapidly with time. Within recent years, for example, minimum ore-grade limits have decreased from about 18% to 10% P_2O_5 (7.9% to 4.4% P); industry now accepts a wider range of lower grade concentrates, and market values of mine products have advanced. No permanent significance can be attached, therefore, to the currently assigned limits of flexibility that define mineability in present market conditions.

Some of the major factors that affect the mineability of phosphates are the geological character of the deposit, ore-to-waste ratio, mining methods applicable, ore quality and grade, concentration ratio, recovery efficiency, and

mine-to-mill transport. Any of these factors can change a phosphate deposit from an economic reserve to an uneconomic resource as well as substantially influence the 'average mining cost' of a deposit. (For a more complete discussion of these factors see Lehr & McClellan 1973.)

In the extensive literature on phosphate mining there are few data on direct mining cost for current extraction methods. One finds an occasional reference to cost data but it is usually an estimate based on fragmentary data or an average over broad cost ranges. Neither basis has much practical value as an economic guideline.

In a US Bureau of Mines survey, Service & Peterson (1967) concluded that no direct mining costs are available although inferences can be drawn by evaluating various phases of the total operation. No real significance can be attached to such 'average mining costs' because of the wide variation in direct costs from mine to mine and other factors already mentioned.

Some comparative mining costs, which are now out of date, were reported by Ruhlman (1958) and provide one of the few examples of published cost figures (see Table 1). In 1967, the US Bureau of Mines estimated an average cost of $1.26/ton of surface mined rock delivered to the mill (Service & Peterson 1967). Everhart's 1971 estimate of direct mining costs of $1–2/ton of ore recovered brackets this earlier figure. Stowasser (1977) states that most US rock is produced for $10–12/ton from old plants and may be as much as $15–20/ton for new plants of marketable rock. These figures are comparable to the $11.75/ton of concentrate calculated by Russell (1976) for South African rock. About one-half to two-thirds of these most recent estimates is direct mining cost; the remainder applies to transportation, milling, beneficiation, and fixed overheads. Underground mining costs are stated to be in the range of $4–5/ton in 1958 and have probably quadrupled in the past 20 years.

TABLE 1

Typical phosphate mining costs

| Phosphate deposit | Mining method | Average 1958 mining cost (US $/ton)[a] | | |
		Overburden removal	Mining and washing	Flotation cost
Florida pebble	Strip	0.30	1.20	1.55
Tennessee brown	Strip	0.40	3.75	
Idaho high-grade	Strip	0.50	3.25	
Idaho high-grade	Underground		4.25	

[a] 1958 Bureau of Mines data from Ruhlman (1958).

FACTORS AFFECTING BENEFICIATION

Many technical methods are used to upgrade phosphate ores to marketable concentrates, but the beneficiation requirements for any given mine operation are largely determined by ore characteristics and the end-use of the concentrates. The limits of commercial beneficiation are restricted by economics rather than technical know-how. Satisfactory upgrading methods exist for nearly every known ore type, but for some the costs may be too prohibitive to consider further development plans.

Since no standard scheme of beneficiation applies to all phosphate ores, there can be no meaningful average cost for beneficiation and its component steps, or its *pro rata* share of total production costs.

Direct costs vary with the combination of methods required by specific ore characteristics (hardness, texture, mineral composition), the required enrichment ratio, and overall recovery ratio.

Numerous upgrading procedures that are used in commercial processes have been extensively described (Ruhlman 1958; Breathitt & Finch 1977) and are briefly summarized here. Physical beneficiation, including grinding, wet- or dry-sizing, desliming, washing, and air classification, is the simplest and most widely used technique. More complex and expensive procedures involving flotation and calcination are required by ores needing high concentration ratios or when thermal treatment is used to change the physical or chemical properties of the ores.

Beneficiation procedures are used to separate the phosphate from undesirable accessory minerals that dilute the ore. The major ore types needing beneficiation are siliceous ores, carbonate ores, and ores rich in clays. Because of the variable composition of phosphate ores, a unique combination of beneficiation techniques is needed for each mine to produce a marketable concentrate of the quality and grade desired with high recoveries of phosphate from the process. This variability of combinations makes an assessment of costs difficult. A rough cost figure for beneficiation can be estimated by doubling the costs of mining and transport (delivery of the ore to the mill). Even this generalization fails if calcination is required in which case another $3–4/ton or more will be added.

In summary, beneficiation costs are essentially process-specific and are difficult to evaluate as averages for the industry because of the variety of the ores treated. Such data are needed but there are inherent risks in using them too strictly.

QUALITY FACTORS OF CONCENTRATE

Concentrate quality is having an increasingly important impact on market value. The single objective of nearly all beneficiation processes is improvement of the P_2O_5 content. Any improvement in other chemical or physical quality factors is more or less incidental. Concern by mine producers over undesired impurities such as Al, Fe, and Mg is mitigated by the lack of market specifications.

Today's more complex fertilizer processes in worldwide use require specific types of raw materials. Not all sources of commercial concentrates are suitable for a particular process and *vice versa*, nor is one particular concentrate broadly suited for all manufacturing markets. Each of the major end-uses—manufacture of wet-process acid, superphosphoric acid, ammonium phosphates, superphosphates and nitric phosphates—has preferred characteristics for the phosphate raw material. The actual economic value of a concentrate is becoming increasingly dependent on end-uses and on the buyer's preference for some particular set of quality factors and not merely its P_2O_5 content.

In various chemical processes, several physical and chemical factors are important. Physical factors such as texture, hardness, porosity, particle size, and crystallinity of the phosphate can directly contribute to difficulties in mining, milling and beneficiation. Chemical factors have a direct effect on the chemical and physical properties of the end products because of their tendency to be passed through the various processes as soluble contaminants. Some of the chemical factors include grade of concentrate and product, the content of fluorine, silica and carbonate in apatite, accessories, the Ca/P ratio, and the content of iron, aluminium, magnesium, sodium, potassium, heavy metals, toxic elements, radionucleides, chlorides and acid insolubles (Lehr 1976). It is apparent from this long list that the principal market specification based on P_2O_5 can be an unreliable indicator of the production quality obtained from various processes using different raw material sources.

TRANSPORTATION FACTORS

Transportation factors that contribute to higher selling costs of the mine concentrate include (1) ore movement from the mine to the beneficiation plant, (2) transport of concentrate products to domestic markets or seaport terminals, (3) ocean transport to export markets or distant domestic markets, and (4) transport of inflowing mine supplies, plant equipment, fuel, and related material needs to the deposit site.

In all these transportation costs impose such rigid limitations on profitable marketing spheres that most authorities consider the collective transportation problems as an initial step in the evaluation of phosphate reserves, and it may be the single overriding factor, despite other favourable aspects of the deposit.

Freight becomes a major cost factor because of the low unit value of phosphate, \$0.05–0.15/kg P_2O_5. The location of nearly all commercial deposits competing in international trade within 160 km of deepwater seaports underlines the importance of location and transportation. High-grade ores that are cheaply mined and require little or no beneficiation can partially compensate for unfavourable location. The recent production in Queensland, Australia, is an example of such circumstances.

Another approach to solving transportation problems is to ship fertilizer products or intermediates that are produced at or near the phosphate deposit. This production may use unbeneficiated or partially beneficiated rock to give a higher valued product so resulting in another potential saving in cost. However, a unique combination of transportation factors will exist for each geographical deposit.

Whether or not a phosphate deposit is profitably located with respect to domestic or international production and end-use markets is determined to a large degree by the distance and means of transport available. Transportation costs can vary from a minimum of \$0.00074/ton km for backhaul ocean shipping to \$0.16/ton km by truck or rail in developing countries (IFDC 1977). Transportation factors can favour seaboard deposits with distant export markets and restrict their domestic market sphere to nearby markets. These same factors can deny export markets to interior deposits, thereby restricting their use to local production or regional markets. The solution of transportation problems is crucial to exploitation problems of major deposits in Africa, South America, Mexico, and Australia.

Market factors

Forecasts in the mid-1960s that the world output of phosphate would continue to expand at an annual rate of 10% to meet expanding food needs (Hignett 1967) have been revised downward as a result of the oversupply in the late 1960s and the sharp price increase during 1974 and 1975. Stowasser (1977) forecasts that growth of US demand for rock will range from 2.1 to 2.3% between 1975 and 2000 while world demand will vary from 3.3 to 4.0%. This means that world demand will rise from 110 Mton in 1975 to 163 Mton in 1985 and to 300 Mton in 2000. About 85% of this production will be converted into fertilizers.

Phosphate rock deposits are widely distributed geographically and 31 countries are producers. However, three countries, the USA, the USSR and Morocco, account for 79% of current production—a situation that is unlikely to change. One analysis of the world outlook (Russell 1976) indicates that US exports have peaked and production increases will barely be sufficient to meet local demand. This author sees a continuing Moroccan domination of international trade as the USSR reduces exports and becomes a net importer by about 1980.

Phosphate rock prices, like those of many other commodities, vary with the ups and downs of supply. In 1970–1971, the price of phosphate rock reached a 20-year low (Table 2) thereby causing all producers except Morocco to stop expansion programmes that exceeded the needs of their home market. The result was a short-lived prosperity boom (from January, 1974, to July, 1975)

TABLE 2

Time–price relationship for phosphate rock

| Year | Average annual price (US $/short ton)[a] | |
	Actual prices	Constant 1975 dollars
1954	5.58	11.82
1955	5.62	11.64
1956	5.64	11.33
1957	5.61	10.89
1958	5.63	10.76
1959	5.54	10.37
1960	5.99	11.03
1961	6.27	11.44
1962	6.27	11.24
1963	6.32	11.15
1964	6.34	11.03
1965	6.50	11.05
1966	6.73	11.09
1967	6.64	10.62
1968	6.12	9.37
1969	5.57	8.12
1970	5.26	7.28
1971	5.26	6.92
1972	5.10	6.45
1973	5.66	6.75
1974	10.98	11.94
1975	22.99	22.99
1976	19.28	18.34

[a] US composite domestic and import free-on-board mine prices (source of data: US Bureau of Mines 1977).

and capacity expansion that has led to the present buyer's market where supply exceeds demand. Present projections (Russell 1976; Stowasser 1977) indicate this condition will continue into the 1980s.

UTILIZATION OF PHOSPHATE ROCK

Historically, phosphate fertilizers advanced from pulverized natural phosphates (e.g. rock, bonemeal) to crude acidulated phosphates and thermally altered apatitic rocks and, finally, to present-day highly refined, water-soluble, chemical compounds. Since the 1930s, advances in mining and beneficiation technology provided industry with low-cost raw materials on which the present generation of advanced chemical processes was based. Emphasis shifted to soluble phosphate compounds based on wet-process phosphoric acid and nitric-acid acidulation routes.

Consequently, the bulk of today's worldwide phosphate fertilizer needs is supplied in formulations comprising water-soluble salts of ammonium or calcium. Such high-analysis refined fertilizers have diminished the use of former lower-grade, less-soluble, phosphate fertilizers. Chemical and thermal fertilizers are produced by various treatments (Fig. 1) and, although many products are made, the bulk of fertilizer phosphate is consumed as a few products (Table 3).

TABLE 3

Most popular phosphate fertilizers

Material	P_2O_5 content (%)
Diammonium phosphate	46–53
Monoammonium phosphate	56–61
Triple superphosphate	43–48
Single superphosphate	16–21
Nitrophosphate	15–30
Phosphate rock	26–31

Direct-application materials

Historically, the use of phosphate rock for direct application has been a subject of much controversy, empirical assumptions, and unpredictable value to agriculture. It suffices to state that phosphate rocks are now known to differ widely in their reactivity or suitability for direct application and that some selection principles have now been developed to guide the choice of rocks (Lehr & McClellan 1972). For illustration, Fig. 2 compares a represen-
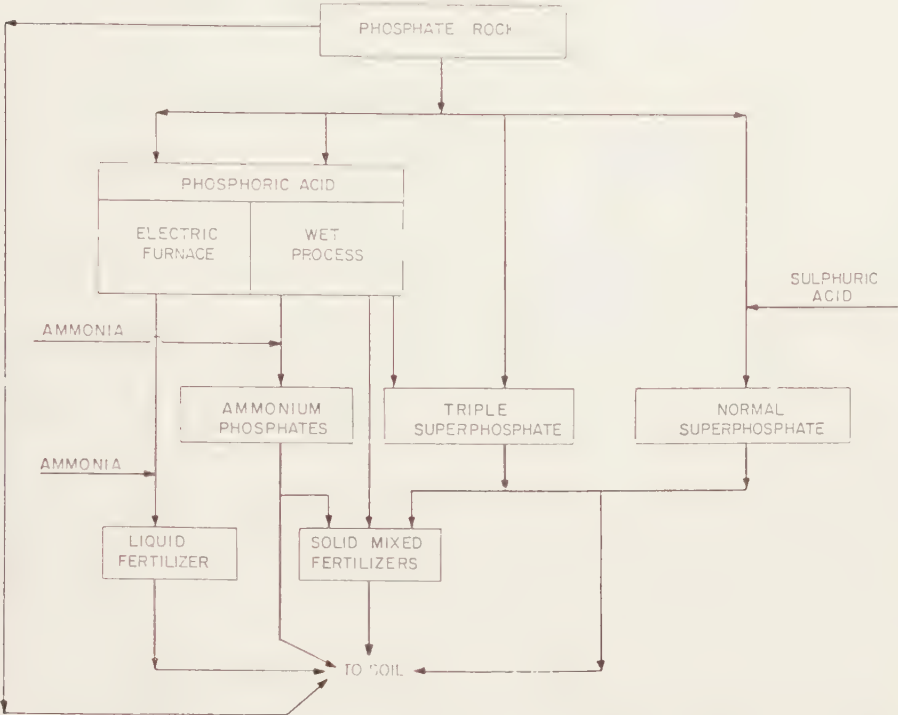
Fɪɢ. 1. Diagram of the various processes for making fertilizers from phosphate rock (UN Fertilizer Manual 1969).

tative series of phosphate rocks on a relative scale of citrate-solubility, which is directly related to the composition of the individual apatite minerals.

The trend towards granulated rocks for direct application introduces some important considerations. The use of granulating agents (such as neutral salts, acids, ammonium phosphate salts, or ammonium polyphosphate solutions) leads to a spectrum of product types. Granulation induced by water-insoluble binders may be irreversible. Granulation induced by partial acidulation or by use of water-soluble phosphate salts leads to hybrid types of phosphate fertilizers, intermediate to ground rock and chemical fertilizers. Each will have different performance characteristics, and this difference should be clearly recognized in evaluation studies now underway. Conventional granulation also reduces the agronomic effectiveness of phosphate rock, but a new method developed by the International Fertilizer Development Center produces 'minigranules' (0.1–0.5 mm) that may overcome application problems.
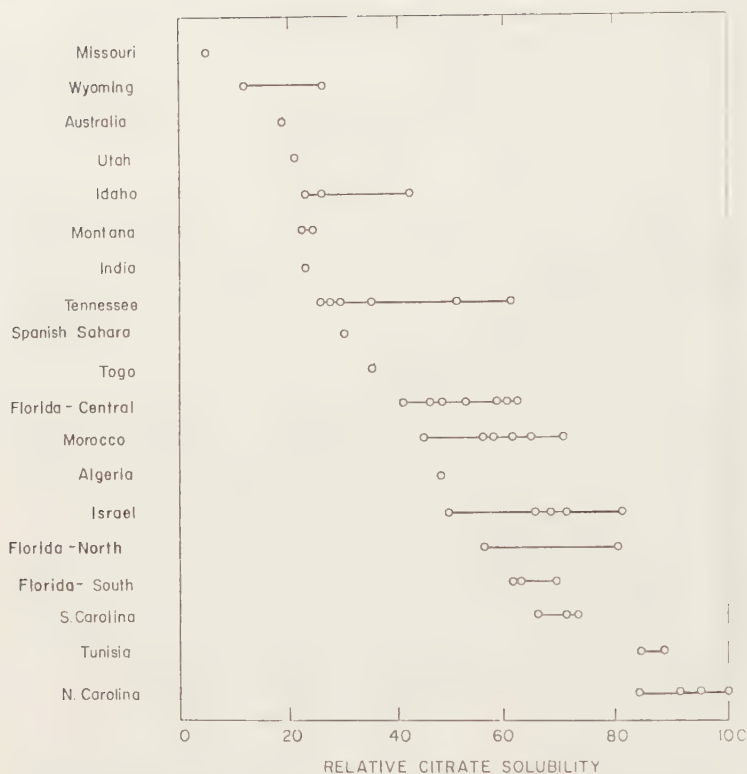
Fig. 2 Relative potential (measured as relative citrate-solubility) of phosphate rocks from various sources for use in direct application as fertilizer.

New direct-application materials in the form of calcined iron–aluminium phosphate ores are now becoming available. Their composition, solubility, and release mechanisms contrast with those of apatitic phosphate rocks, and granulated grades may suffer a serious decrease in availability owing to reversion reactions initiated by salt binders.

Thermal phosphate products constitute a final category of modified natural phosphate rocks. Various inorganic reactants may be used to promote decomposition of apatite, to evolve fluorine, and to cause calcium and phosphate to recombine as more reactive compounds or vitreous phases. The important types of reagents that have been so used are listed in Table 4. As many of these occur in natural mineral associations in various phosphate rocks, some marginal rocks may be most efficiently used by this thermal-processing route. Despite the wide choice of reactants, products can be conveniently grouped on the basis of structural form and composition, as

TABLE 4

Some types of thermal phosphate products

Theoretical composition	Types of materials	Reagents
$(Ca,Mg)_3(PO_4)_2$	Tricalcium phosphates	(None)
$Ca_4O(PO_4)_2$	whitlockite; glasses; hilgenstockite basic slags	Alkaline earths
$CaNaPO_4$ $CaKPO_4$	Rhenania compounds	Alkalies
$Ca_7P_2Si_2O_{16}$ $(Ca,Mg)_7P_2Si_2O_{16}$ $Ca_5Na_2(P,Si)_4O_{16}$	Nagelschmidtite	Silica Mg silicates
$Ca_5P_2SiO_{12}$	Silicocarnotite	Silica Silicates
$Ca_{(\frac{1}{2}m+1)}(P_mO_{(3n+1)})^{-(n+2)}$	Poly- and meta-phosphates	Phosphates
Ca_2ClPO_4 Mg_2FPO_4	Chlorospodiosite Wagerite	Halides

TABLE 5

Reagents for thermal phosphates

Silica types	Phosphates
Quartz, opal, chert	H_3PO_4
Feldspar (Na, K, Al silicate)	Alkali phosphates
Olivine, serpentine (Mg silicate)	$AlPO_4.nH_2O$
Alkali metals	Alkaline earths
Carbonates (Na, K)	$CaCO_3, CaMg(CO_3)_2$
Sulphates (Na, K, NH_4)	$CaSO_4.2H_2O$ (gypsum)
Silicates (Na, K type)	$Mg(Na,K)_2(SO_4)_2.4H_2O$
Hydroxides (Na, K)	$CaCl_2.6H_2O$
	$MgCl_2.6H_2O$

illustrated in Table 5. Such thermal products, although of inferior grade to chemical fertilizers, retain essential secondary and micronutrient credits from the precursor rock.

Chemical fertilizers

The manufacture of phosphate fertilizers now consumes about 90% of the phosphate rock raw material using the wet process with H_2SO_4, HNO_3 or H_3PO_4.

Unlike direct-application phosphate sources, wet-chemical processes are highly sensitive to chemical impurities in raw materials. A combination of problems arises concerning processing steps, corrosion of equipment, losses of P_2O_5 by precipitation, lower production rates, and quality of final products. Undesirable precipitates in phosphoric acid are formed in direct proportion to the concentrations of Al, Fe, Mg, K, Na, Si, F, Ca and SO_3. Most acid producers are aware of these precipitation problems and use criteria other than P_2O_5 grade to select raw materials for their processes.

Any delayed or deferred effect of the group of chemical impurities just cited for phosphoric acid becomes a serious problem during the preparation of ammoniated products (mono- and di-ammonium phosphate, ammonium polyphosphates). Here, however, the precipitation processes involving Al, Fe, Mg, alkalies and F lead to insoluble phosphates, many of which contain NH_3 as well.

The increasing occurrence of these phases in ammonium phosphate products can lead to drastically altered physical and chemical properties of products. Formerly, mono- and di-ammonium phosphate products prepared from premium-quality acid were nearly homogeneous crystalline compounds. This is not the case with impure merchant-grade wet-process phosphoric acid reagents.

The process chemistry of superphosphates and product compositions are likewise affected by the cited group of chemical impurities—primarily Al, Fe (iron(II) and iron(III)), alkalies and Mg. Perhaps no other chemical fertilizer type has undergone such a major change in product composition in the past decade due to the use of by-product sludge acid, lower quality phosphate reagents, or both. The traditional component of superphosphate—monocalcium phosphate, $CaHPO_4.H_2O$—is being displaced by a series of Fe, Al, Mg phosphates that have precipitated in commercial processes and now are marketed in superphosphates. As most of these compositions are citrate-soluble, agronomic performance of these superphosphate products has not been seriously impaired. Superphosphates may become increasingly attractive as outlets for phosphate raw materials of marginal chemical quality.

The risk of dissolved metal impurities passing through is greater in nitric-acid acidulation routes, because there are generally no intermediate precipitation stages which might effect their elimination. The major penalty

of using phosphate rock reagents of marginal chemical quality concerns product compositions. Most metal impurities tend to precipitate as citrate-soluble and insoluble phosphates, many of which insolubilize some NH_3 as well. Although the agronomic implications of the compositional change in products has not been resolved, there are obvious marketing penalties depending on the particular control methods in force.

SUMMARY

The many economic and technical factors that affect the utilization of phosphate rock which we have mentioned indicate the many evaluation steps that follow the initial discovery of an 'ore'. The success of the worldwide phosphate industry indicates that the requirements of these factors can be met successfully at numerous sites.

The present challenge is to continue innovative applications of existing technology and to develop new technology to ensure an adequate, inexpensive supply of a critical food nutrient to help meet world food demands. The essential goal of this process is to produce fertilizer that meets the needs of crops at prices farmers can afford.

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Discussion

Brydges: Is it likely that the price of phosphate will rise as the cheap and more available sources are depleted within the next 20–30 years?

McClellan: I imagine that the price will continue to rise.

Brinck: No. You quoted the cost of rock (see Table 2) in constant 1975 dollars. One should not do this because the world economy during the past 50 years has been on a gold-exchange standard which is, after all, a mineral commodity. As I described, the price differences between mineral commodities tended to develop in line with the cost of mining gold. From 1933 to 1971 gold was mined at \$35/oz (\$1.45/g). Converting this price back into constant dollars of the 1920s or 1930s one can see that mining costs decreased tremendously during this period.

McClellan: The point I was trying to make was that in 1970/71 the price of phosphate rock reached an all-time low and constant dollars were arbitrarily selected for comparative purposes.

Brinck: Certainly, the late 1960s and early 1970s were trying times for the phosphate industry. But the price was not as far out of line with the average cost of the mining industry in 1971/72 as are the present prices which tend to follow the price of gold and petroleum. For an economic assessment of mineral resources one has to take this into account and not make comparisons with 'the' constant dollar value.

The price in dollars may go up but the value will not. The present worldwide inflation is largely a consequence of the fact that the prices of some important mineral products are no longer related to average production costs and of the lack of a real internationally accepted monetary standard. Many nations which were accustomed to the convertibility of the US dollar into gold became unsettled when the gold price began to slip away from the dollar value in the late 1960s. Many of our difficulties over the past 4–5 years stem from

the official termination of the gold-exchange standard in August 1971.

Tinker: I get the impression that the phosphate industry will change during the next decade or two—not so much because of a shortage of rock but because perhaps one or two suppliers will exert a stranglehold on the export trade or because many countries may want to use phosphate themselves rather than export it to developed countries to have it converted into superphosphate and then have to import the product.

McClellan: I am inclined to agree; but I don't think the changes will be as dramatic as have been intimated. Phosphoric acid plants will still operate in Europe! But national long-range policies will probably result in some changes.

In September 1976 the Moroccans met six other African producers in Dakar to try to establish a coordinated plan for selling rock. As far as I know, this has not been formalized into an OPEC-type organization yet and it may never be so because one advantage of high prices for phosphate rock has been the incentive to prospect for phosphate rock. This has encouraged, for example, the development of the Queensland deposits in Australia, and spurred the Jordanians, Egyptians and others to develop their phosphate industries. The position of such countries might not be quite as strong as that of Morocco but it will be important, particularly for Europe.

Arthur: I should have thought that the owners of the Moroccan deposits would be extremely cautious of attempting to manipulate the market in phosphate rock supply: one can see clearly the effects that their recent pricing policy has had on use. The industry is still recovering from the material depression of phosphorus use arising from the massive rises in price.

McClellan: But other factors are involved.

Arthur: Of course. Very large deposits of phosphorus are found outside Morocco, notably in the Kola peninsula in the USSR and in Florida.

Loughman: In Western countries phosphorus has been added to the soil for many years and in some cases it is building up in the soil since, in certain conditions, the crop takes out less than the amount put on (even allowing for run-off). So even if the supply of phosphate becomes short, the soil will contain a 'bank' of phosphate.

Kabbaj: To the mineability factors that Dr McClellan cited, I should add two more. One is environmental: waste disposal and land reclamation when mining is complete. The second is a critical factor—the supply of water for phosphate mining—both in wet areas and in dry areas. It is a severe limiting factor for the future growth of the industry.

Brydges: I am getting confused with figures. According to Dr Brinck we have plenty of phosphate reserves but Dr McClellan talked about 1.4×10^{11}

tons of phosphorus and, by the year 2000, a demand of 3×10^8 tons (300 Mton) a year; that means enough reserves for 30–50 years. Then there are suggestions that the Moroccans have the market cornered. Is phosphorus like oil in that we had 500 years' supply of oil 20 years ago but now we are nearly out?

McClellan: In my opinion, there is plenty of phosphate; as there are 31 countries that produce phosphorus commercially (see p. 50), alternative sources do exist (e.g. in Australia, Jordan) and will be developed. If the price becomes sufficiently high, other deposits will be brought into production, even at considerable expense in most cases.

Brinck: I agree. South Africa, for instance, produces phosphate at a high cost; as far as I know, the South African government decided to bring the Phalaborwa deposit (see p. 27) into production for reasons of national security, long before the oil crisis. They knew their position in the world and were prepared to pay more to guarantee their supplies.

McClellan: That attitude is important in developing countries, too. Dr van Wazer mentioned the export of food. Many developing countries have no interest in receiving either food or fertilizer from outside. According to their approach they should be in equilibrium with their own resources. This may have some small-scale effect because in general such countries are small consumers.

Shaw: Besides national security, another reason why some countries produce their own phosphate at high cost is that they are prepared to pay that cost to conserve their foreign currencies. This may become an increasingly important factor.

McClellan: Currency problems are always involved. Brazil is a perfect example; economists there projected that by 1980 they would be spending US $1000 million a year on import of fertilizer and they don't have the currency.

Loughman: The high contribution to costs from energy-intensive transport might justify a shift to low-bulk materials combining phosphorus, nitrogen and so on (e.g. phosphoric triamide, $PO(NH_2)_3$). Many countries, for instance East Germany, are showing interest in this type of compound. Nothing is known about the metabolism of these compounds except that they seem to be broken down to orthophosphate.

McClellan: There has been a detectable shift, but in the other direction, away from what we describe as 'gold-plated fertilizers' (e.g. phosphonitrilic compounds such as cyclic $[-N=P(X)_2-]_3$ compounds) to lower grades of conventional fertilizers, triple superphosphates, mono- and di-ammonium phosphates etc., because impurities that occur in the rock are left in and reduce the grade of the product.

Loughman: Even though that means the transport of a lot of waste material?

McClellan: The general trend is to solve the transportation problem as close to the mine as possible by trying to eliminate the moving of non-productive material.

Arthur: A primary function of the phosphorus fertilizer industry is the redistribution of the element. Fig. 1 depicts, for ammonia and potassium as well as phosphorus, the stages involving processing and storage that are interspersed between transport operations. In general, as phosphorus ores are not found in places where food is ultimately wanted, the industry is confronted with many transport, processing and storage operations. The logistical make-up of the industry determines the economics and leads naturally to questions such as where is the processing best done, at the mine or where the food is wanted? As part of the answer, one has to consider the bulk of the materials being carried and what can be done about that.

Fig. 2 shows how phosphate rock can be processed, illustrating the gain in concentration of phosphate. Acidification of the rock gives various products depending on the conditions and the acid used; the increase in phosphate concentration in triple superphosphate represents a saving in bulk, and similarly for the monoammonium phosphate. Heat treatment to give phosphorus itself results in an enormous (seven-fold) gain, but preparation of Rhenania phosphate gives a loss in that respect. Decisions about location and
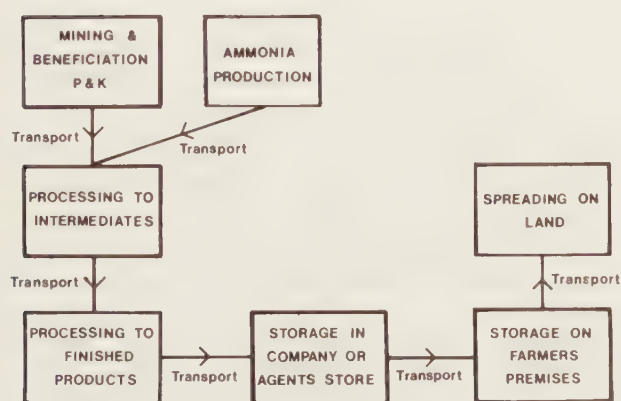
FIG. 1 (Arthur). Transport chain for phosphate (P) from rock to use as fertilizer, and for potassium (K) and ammonia.
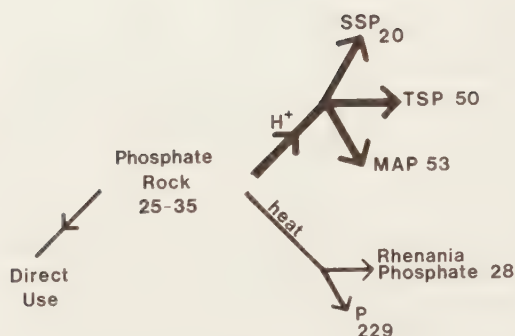
FIG. 2 (Arthur). Gain in concentration of phosphate (numbers refer to % P_2O_5 content; for conversion factor see p. 50) on processing rock: H^+, acidification; SSP, single superphosphate; TSP, triple superphosphate; MAP, monoammonium phosphate.

selection of manufacturing processes are therefore fundamental to the economics of the industry. Phosphoric acid (with 50% P_2O_5) and ammonium phosphate are good vehicles compared with phosphate rock for transport of phosphorus and are already used commercially in this way.

Probably the most used step for making phosphate rock available is dissolution in sulphuric acid to make impure phosphoric acid and calcium sulphate. This is an extremely complicated reaction and it is worth considering the source of this complexity. Why is it so difficult to predict the phosphates? First, the course of this highly exothermic reaction between a solid and a liquid depends greatly on the source of rock. Secondly, the process is dominated by the chemistry of calcium sulphate, which is discharged as a by-product in various stages of hydration, either as gypsum or as hemihydrate (these forms are not in thermodynamic equilibrium), and by the way it crystallizes, the size of the crystals and how large they grow. More often than not, overall plant capacity is determined by these factors. Thirdly, probably the most important factor is the impurity of the mineral phosphate. Table 1 summarizes how impurities can effect the processing of the rock. Note the number of impurities, the amounts of which are highly variable, and the complicated way in which they can interact and affect the processing of the phosphate rock. Silicon and fluorine are especially important. In particular, these impurities can affect the way in which the calcium sulphate is precipitated out and how its crystals grow. It is a great over-simplification to assume that phosphate rock is just orthophosphate and one need only know the BPL or the P_2O_5 content. That is not so. For example, if one does not take great care during beneficiation about a minor component like chloride one

TABLE 1　(Arthur)

Effects of impurities in phosphate rocks on the production of phosphoric acid

Impurity	Effect
$CaCO_3$	(i) Wastes acid (ii) Foaming due to CO_2 prevents wetting of rock
Complex organic matter	Reduces surface tension of reaction slurry and stabilizes foam caused by gas evolution; hazardous if P_2O_5 products later mixed with nitrates
Silicon Fluorine　} Alkali metals	Resulting alkali fluorosilicates cause scaling
Iron, aluminium, magnesium, sodium and potassium	React with anions—phosphates, silicates and fluorides—to give sludges which complicate acid storage and shipping: water-soluble P_2O_5 component of acid decreased
Magnesium fluorosilicate, octahedral crystals, e.g. $Ca_3Al_3(RE)SO_4F_{13}.10H_2O^*$	Hinder filtration of calcium sulphate
Many	Change kinetics of crystal growth of $CaSO_4$: size, distribution and shape of crystals may affect filtration rate and efficiency of P_2O_5 recovery
Chloride	Corrosion of stainless steels

* RE is a rare-earth element.

may soon have a badly corroded phosphoric acid plant. If the chloride cannot easily be separated from the phosphate rock, the phosphoric acid plant will have to be rebuilt with expensive stainless steel to make it resistant to the chloride. Valuation of mineral phosphates is complicated and thorough analytical and continuous pilot-plant facilities are needed for testing out these variables before release of the material to the large plants operating in industry. Use of phosphate rock in a commercial plant without proper testing can lead to very large losses in production capacity. Fisons has long experience of testing phosphate rocks for their suitability for production of superphosphates and phosphoric acid. For instance, about 7–8 years ago we tested the new Sahara Bu-Craa deposits where there are reserves of about 1.6 $\times 10^9$ t and at about the same time we tested deposits in the Lady Annie Seam

in Queensland which contain about 2.5×10^8 t. Both surveys were done on behalf of the owners before exploitation of the deposits.

R. J. P. Williams: It seems that the chemist can make no new inventive contribution to the production of phosphate from the ore; industry is satisfied with the wet process of adding sulphuric acid. But chemical problems in handling remain; these are problems of separation, crystal growth, the interaction of impurities, and the recognition of the crystal phases that can interfere with the process of precipitation and crystal growth.

McClellan: In addition, the impurities are important for the quality of the product because they might preclude its being used in a particular way. For example, the presence of iron, aluminium and magnesium is extremely undesirable in these acids if they are to be converted into superphosphates (they cause the product to be sticky) or ammonium phosphates (in which case they cause precipitation of insoluble compounds).

Nielen: One should perhaps distinguish the different applications of the phosphate rock—in agriculture for fertilizer, and its 'technical' uses (e.g. as oxides, sulphides) for pesticides and insecticides, etc. For these latter uses, two methods of preparation exist: first, the thermal way, from the crude phosphate to elemental phosphorus and then, by oxidation, to oxides of phosphorus, phosphoric acid and salts of phosphoric acid; and, secondly, the wet process. The critical impurities are different for both routes. For the thermal way, impurities like zinc and magnesium are important but organic impurities, which are burnt, are not. For the wet process, organic impurities are critical; they colour the phosphoric acid and also lead to foaming (as Dr Arthur noted in Table 1). From the chemical point of view, much research needs to be done, as the question of which phosphate rocks should be won depends on the effect of impurities. At present the rock phosphate with the highest P_2O_5 content is the most economic one. Developing countries might benefit more from the import of technical knowledge about not only how to win the rock phosphate but also how to produce phosphorus products. Some countries (e.g. Morocco) have begun to do this, exporting not only crude phosphate but also phosphoric acid. This trend may become more pronounced.

Shaw: It is cheaper to transfer know-how than to transport rock.

van Wazer: Owing to its crystal structure and the particle size apatite can bear many elements. It seems plausible that one of the benefits of using wet-process phosphoric acid or superphosphates in fertilizers is that the various essential trace elements are transferred to the soil. Several unwanted elements (e.g. cadmium) will also be transferred, of course, but the plants in most cases do not pick up these undesirable elements. Animals need about 25

different essential elements, about half of which are trace elements.

R. J. P. Williams: Where does man get cadmium from if he does not get it from plants? Protection against cadmium apparently exists even in bacteria, which can synthesize proteins that bind cadmium.

van Wazer: We obtain some from food because the chemistry of cadmium is similar to that of zinc and the two elements are often associated with each other. We also obtain some from galvanized pipes and other sources.

R. J. P. Williams: But the protection mechanism is much older than this sort of technology.

van Wazer: There is a protection mechanism, but in field tests (reported at a Tennessee Valley Authority meeting on *Trace Elements* in 1977) zinc was picked up to a much greater extent than cadmium.

Bowman: Marine organisms accumulate cadmium.

R. J. P. Williams: Yes; shell-fish and similar animals do but plant life apparently does not need to be well protected against cadmium.

McClellan: That depends on the species. Leafy plants tend to accumulate it.

R. J. P. Williams: The special mechanisms for chelating cadmium that exist in animals also exist in bacteria.

Returning to the matter of reserves, is it clear that they are totally adequate for our projected needs, and is it then a question only of whether the phosphorus gets to the places where it is needed? If the USA will not be able to export, if the USSR is already stopping the export of phosphate and if Morocco then has a monopoly, what is the significance of these events for the population of the world at large?

Bowman: If we compare Dr Brinck's figures for reserves (given in terms of P) by multiplying them by six with those quoted by Dr McClellan (given in terms of rock), we find that the present rate of consumption should be possible for about 2000 years. But even if the rate of population increase falls to zero immediately the present world population will double by the year 2000. If that population is to live at anywhere near the level that we consider satisfactory in the developed countries, agricultural production in about two thirds of the world has to increase markedly and, therefore, consumption has probably got to treble or quadruple in that same period. If we assume, also, that the efficiency with which we use that rock will deteriorate, the estimate of 2000 years' supply drops to about 200 years'. Are we satisfied to consider the provision of phosphorus for the next 200 years only or do we want to take a longer outlook for the future existence of man? We cannot afford to be complacent about future supplies of phosphorus.

Perhaps of more immediate concern is the possible shift in the location of

processing from the developed countries to the countries with the rock phosphate. Such a shift is likely to have a major effect on the availability of supply (certainly to Europe) and on the cost of phosphorus fertilizers to Europe.

R. J. P. Williams: What is the situation with regard to a country like India? Does the adequate supply of phosphorus depend critically on the country's internal economy?

McClellan: India has enough indigenous materials either in production or coming into production to meet its requirements.

Bowman: The reason why I suggested a possible decrease in the efficiency with which phosphorus is used is that countries in the developing world will not necessarily be able to upgrade or process rock phosphate to the same extent as developed countries can. Those countries that want to use certain types of phosphate may not be able to afford the improved technology needed to produce them.

McClellan: I don't agree. Many developing countries have an interest in direct application of the rock, a use for which, in general, no beneficiation is needed. The rock is dug up, ground, carried to where it is needed and put back on the soil; the conservation of resources, if you want to look at it that way, is probably as good if not greater than that in some developed countries.

R. J. P. Williams: Is it true then that Europe will be a vulnerable area as far as phosphate is concerned?

McClellan: With present trade patterns that is probably true; to a certain extent S.E. Asia will be, too, although their predicament depends on what happens about the Australian deposits. But we must remember that, if the demand is there, alternative sources can and will continue to be developed (as happened as a consequence of the recent price rises). I once plotted the rate of discovery; that is, I took nominal resources from the time they first appeared in the literature around 1900 as 'world phosphate resources' and found that deposits which are 'reserves and resources' are being discovered at a rate faster than the rate of consumption. If that trend continues, one could conclude that Europe will have alternative sources, whether they be in Latin America, Australia or elsewhere. And that negates the idea of one country or small group of countries dominating the market.

Larsen: Paradoxically Australia faces a phosphate problem in spite of the discovery of large deposits in Queensland. At a workshop on 'Prospects of Improving the Efficiency of Phosphorus Utilization' (in Armidale, New South Wales, 26–28th August 1976) it became clear that the producers of phosphatic fertilizers in Australia refuse to use the new rock phosphate because its impurities such as sesquioxides (Fe_2O_3 and Al_2O_3) caused nothing but trouble

in test runs. They are now planning, as a trial, to export it to S.E. Asia for direct application which is possible because the acids in the soils there can mobilize the phosphate in the rock. So the Australians will still have to import high quality phosphate.

Modern mankind's influence on the natural cycles of phosphorus

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Abstract   When the molten surface of the earth solidified over 4×10^9 years ago the quantity of phosphorus to be contained in the storehouse of the new planet had already been resolved. The phosphorus was locked in an igneous lithosphere as orthophosphate. With the advent of the first primitive rainstorms the slow endless process of liberating the phosphorus from the igneous rock strata had begun. It required about 3×10^9 years for this process to supply enough soluble phosphates for the seas of the earth to become saturated with respect to apatites. Today slightly more than half of the phosphate is contained in sedimentary deposits.

The established phosphorus cycles of the earth were almost independent of the activities of mankind for more than 4×10^9 years. Only in the past 200 years has the influence been worthy of consideration and as late as the 1960s too few reliable data were available for us to assess the status of our activities on the natural cycles. Today a reasonably clear picture is emerging.

Before a meaningful assessment of mankind's influence on the natural cycles of phosphorus can be made it is necessary first to develop a baseline from which judgements can be drawn. To understand man's influence we must first understand what occurred before man exerted an influence on the phosphorus cycles of the earth.

There is perhaps no better way to understand the current status of phosphorus than to start at the beginning of phosphorus on earth and trace the history of the element up to the present. By this approach it will be necessary to establish the required baseline for judgments. The influence of man can then be superimposed on the cycles which were occurring before his entry on earth or his influence can be subtracted from the current cycles. Both approaches shall be used, depending on which seems to yield the clearer overview.

THE BEGINNING

The earth was probably a molten sphere about 4.3×10^9 years ago. As it cooled the surface solidified to an igneous crust, ruptured and was perforated by outgassing and flows of magma. Even before the crust began to form, the earth's generous allotment of phosphorus had been delivered. The phosphorus was to be imprisoned as orthophosphate in dense, impervious, igneous rock (Griffith *et al.* 1977). As cystallization and differentiation progressed some localized enrichment occurred but most of the phosphorus was to be more or less uniformly distributed throughout the lithosphere at a concentration of about 1 part in 1000.

When the surface cooled below the boiling point of water, liquid water first trickled over the steaming hot rocks while minute quantities of igneous phosphate rock dissolved in the nascent hydrosphere. Once the crust of the earth became cool the oceans of the earth formed quickly, taking no more than about 3×10^8 years to reach a volume approaching their present size (Arrhenius *et al.* 1974). The oceans formed so rapidly compared with the rate of weathering of igneous rocks that the primitive hydrosphere contained almost no phosphorus. About 3×10^9 years later enough igneous rock had been crushed, ground, crumbled and weathered to release enough phosphorus to saturate the oceans with respect to calcium orthophosphate and the natural cycling of phosphorus was underway.

Before the oceans became saturated with orthophosphate they acted as a gigantic sink for phosphorus. They quickly gobbled up most of the phosphate, holding it in solution so dilute as to prohibit large populations of primitive life forms from developing. Only small pockets of primitive life existed in areas which captured some of the phosphorus as it flowed toward the seas.

After 3×10^9 years the seas finally ingested enough phosphate to saturate the waters. Any new phosphorus carried to the seas in run-off no longer remained in solution but precipitated as sedimentary phosphate deposits. The waters of the earth had moved from a deficit phosphorus inventory to a surplus status and sufficient phosphate was available to be shared with a developing biosphere. The stage was set for the explosive production of life which was to occur in the Cambrian period (see Fig. 1).

The Precambrian deposits of sedimentary phosphate rock are small (McKelvey 1973) but during the late Precambrian the sedimentary deposits began to increase in size rapidly. Most of the earth's reserves of phosphate ore were deposited throughout the Palaeozoic, Mesozoic and Cenozoic eras.
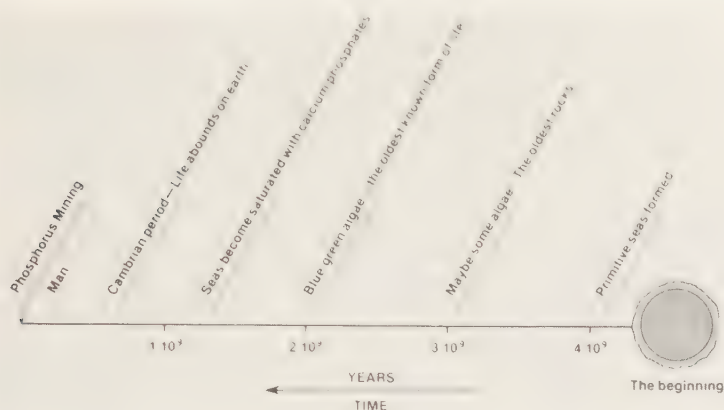
FIG. 1. The history of the earth.

THE GIANT SEDIMENTARY DEPOSITS

Throughout much of their later history, the land masses of the earth have been periodically inundated by encroachment by the oceans. The inland seas which formed as a result of the invasions of the oceans between 2×10^8 and 6×10^8 years ago became highly eutrophic with respect to phosphorus. The life forms living in and around the shoreline of the seas aided in collecting and transporting phosphate to the shorelines where it concentrated as the giant sedimentary ore deposits mined today.

Whether all the ore deposits formed as a direct result of life is subject to considerable speculation and some of the phosphorus was surely precipitated by chemical action only. But there is no question that life forms played an essential role in many of the larger deposits. There is also no doubt that the inland seas became highly eutrophic and that the stench of dying blue-green algae permeated the primaeval air millions of years before the advent of man. The oldest definitely established life on earth occurred about 2×10^9 years ago. The remains of this life are found in the Gunflint Cherts discovered by Tyler & Barghoorn (Zverbles 1975). The oldest known form of life is the primitive blue-green alga (Schopf 1974).

The enormous size and the abundance of fossils contained in the sedimentary phosphate ore deposits also attest to the widespread eutrophication of the ancient inland seas. Emigh (1972) estimates the known world reserves of phosphate rock as 1.30×10^{12} ton (1.32×10^{12} tonne). McKelvey (1967) states that the reserves are several hundred thousand million tons and even the most pessimistic estimate is 25×10^9 tons. Regardless of the accepted figure, the phosphate deposits are adequate to supply the needs of man for hundreds to thousands of years. There is no shortage of phosphorus on earth.

About 85% of the phosphate rock currently mined comes from the giant inland sea deposits. Most of the remaining 15% of igneous origin is mined on the Kola peninsula in the USSR. The phosphorus in the igneous ore deposits was probably concentrated exclusively by differentiation.

THE CYCLES BEFORE MAN

At least 100 million years before mankind exerted any influence on the cycles of phosphorus a pattern had already been established. Phosphorus was continuously leached from igneous rock as the rocks were weathered to sedimentary deposits and this additional phosphorus flowed to the seas which had long since become saturated with phosphorus. Each new addition of phosphorus to the seas caused a similar quantity of phosphorus to precipitate as a sediment. If the precipitate formed when an inland sea had invaded a land area, the new sediments became land-locked. The new land-locked sedimentary deposits are more easily leached than igneous rocks from which they are derived. When the seas recede sufficiently to expose the new sediments to the greater solvent action of fresh water, the sediments begin to weather and the cycle is complete.

Life follows life and phosphorus follows phosphorus. Because phosphorus is vital to all life and the food chain of the biosphere depends on one organism devouring another to survive it is not difficult to understand how living organisms aided the formation of the giant deposits. Organisms which feed on the flora migrate to the food supply bringing more phosphorus with them. Their waste products and remains increase the localized quantity of phosphorus and each cycle causes an increase in the size of the deposit.

Finally the forces tending to disperse the phosphorus and the forces tending to collect the phosphorus reach a mobile balance which remains more or less stationary until a geological event of sufficient magnitude disturbs the balance. Once disrupted the cycles may return to the same localities or conditions may be more favourable in some new areas.

Best estimates of the cycle time of phosphorus in the oceans today are in the range of 50 000 years (Tromel 1932). This is a short period compared to the 3×10^9 years required to saturate the oceans for the first time. It is also much shorter than the time needed by most of the other salts of sea water to complete a cycle. The reasons for the increased rate of cycling are many but a major cause is the more rapid weathering and leaching of sedimentary deposits than of igneous deposits. Moreover, the action of all life forms, including man, causes the rates to increase. It is estimated that marine birds may remove as much as 5×10^{10} g of phosphorus from the oceans each year.

If this value is correct, bird life alone could cause a cycle of ocean water to occur in about 2×10^6 years.

FRESH WATER CYCLES

As a result of mankind's recent preoccupation with phosphates in the fresh water resources it is necessary to understand the magnitude and rates of the fresh-water cycles before attempting to draw conclusions about the role of phosphorus in lakes and rivers. Because phosphates are nutrients capable of causing overproduction in some bodies of fresh water they have been prohibited from being used in detergents in some areas of the world. How general are the problems with phosphates in fresh waters? I shall attempt to answer this question after I have presented the pertinent data.

First consider the water cycles themselves. Each year the land areas of the earth receive 24 000 mile^3 (about 108 000 km^3) of precipitation. About 62% of this water is evaporated and 38% flows into the oceans as run-off. The lakes and rivers contain about 30 300 mile^3 of fresh water with lakes holding about 99% of the total volume. The fresh surface water of the world is recycled about every 3.3 years. This means that as an average the world's per capita supply of fresh surface water is 1 115 000 ft^3 and that the supply is renewed every 3.3 years (Todd 1970).

A very small fraction of the earth's fresh water is contained in surface waters. About 0.61% of the total hydrosphere is contained in fresh water aquifers and 0.009% is contained in lakes with only 0.0001% flowing in rivers. The cycle time for lakes may range from weeks to hundreds of years depending on the size and location of the lake. Rivers, on the other hand, cycle rapidly, usually in only a few days even for the larger and longer streams.

Most of the world's major lakes are located in remote, almost uninhabited areas. Of the world's 30 major fresh water lakes with an area of 1000 mile^2 (2600 km^2) or greater only 10 are located in areas where the population density is greater than 10 inhabitants/km^2. This probably occurs as a result of the manner in which natural lakes are formed. Most have formed as the result of some bold geological event such as glaciation, earthquakes, volcanic eruptions—in which conditions mankind traditionally has encountered difficulties in surviving.

POPULATION DISTRIBUTION

Fig. 2 shows the distribution of the population of the earth. Mankind inhabits but a small portion of the total land area. For the most part he has

FIG. 2. The distribution of population on the earth. (Rand McNally–No. 77-S-26).

settled along the coastal plains and along the great rivers but he has shown no great preference for lakes.

Many factors have contributed to this distribution. Temperatures both hot and cold have been a factor and man has not settled densely in areas where either extreme persists. Historically man has settled in areas where fresh water and food were plentiful. This implies that the areas were rich in natural phosphate supplies and are where life thrived before mankind usurped the areas.

The man-induced problems associated with phosphates in the fresh-water resources occur only at those points on earth where lakes, phosphates, and people interact. There are no problems associated with phosphates in the rivers of the earth and the problem points of the world are isolated systems rather than a general worldwide condition. No worldwide phosphate problem exists. No nationwide phosphate problem exists. The limited number of problem areas are confined to community dimensions.

THE IMPACT OF MAN

By the time man appeared on earth the sedimentary deposits were established and the major cycles had been operative for millions of years. Early man occupied an infinitesimal fraction of the total existing biosphere and he was more a victim of the cycles than a contributor to them. Most of his time during the first million years was spent in a manner similar to that of the existing animal life, striving to establish a dominance in the food chain. It is safe to assume that during this time his influences on the cycles were too insignificant to be considered even an influence.

It was not until the 19th century that man made any conscious effort to use the cycles of phosphorus to his advantage in any but a secondary way. He learned that by extracting phosphate ores he could in effect inject himself into a food chain which existed several hundred million years before. The ancient life could be made to live again in the form of vegetables, livestock and people.

The total phosphate rock mined in the history of the earth is less than 2×10^9 tons. This is less than 100 lb (45 kg) of phosphorus per capita for the current population of the earth and yet this small quantity of phosphorus has allowed the population of the earth to quadruple while more food has been available than for any of their predecessors.

Despite the advantage to which phosphorus has been used it is doubtful that man has yet made a significant contribution to the cycles. The 2×10^9 tons of mined rock is less than 0.15% of the known reserves of phosphorus ore and is less than 0.000 05% of the earth's total phosphorus.
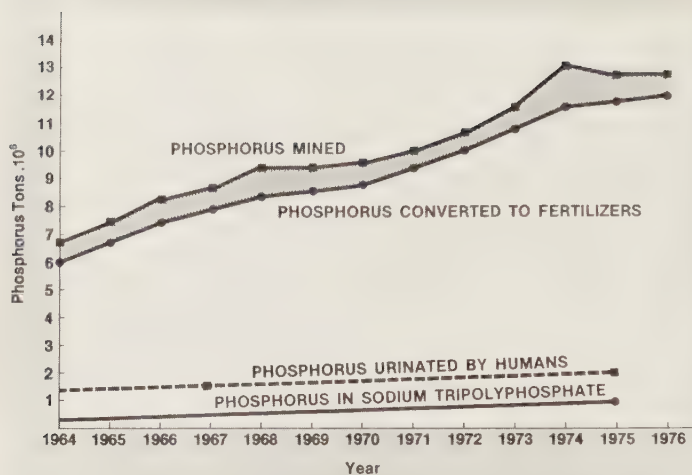
FIG. 3. The amount of phosphorus mined and used between 1964 and 1976.

Fig. 3 illustrates the phosphorus equivalent of phosphate roch mined between 1964 and 1976 inclusive (British Sulphur Corporation 1977), showing the quantity of phosphorus converted into fertilizer. All other phosphorus products are made from the amount of phosphorus represented by the difference between the curves. Detergent phosphates make up about 60% of the differences with mineral supplements for stock feed taking most of the remaining phosphorus. The quantity of phosphorus urinated by the people of the earth is more than twice the quantity used in detergents.

Another way to consider the quantity of phosphates produced is by the energy consumed by the phosphate–phosphorus industry. In 1974 more phosphate rock was mined than in any other year in history. The industry consumed less energy than the equivalent of three million barrels of oil. More oil than this was spilled in 1974. The phosphate–phosphorus industry is a relatively small industry.

The USA supplies about 40% of the world production of phosphate rock. In 1976 the value of that rock was less than 0.04% of the gross national product of the USA.

Modern man has had only slightly more influence on the total phosphorus of the earth than his prehistoric ancestors. If man has made a significant alteration in the cycles of phosphorus it must have occurred in the cycles of the fresh surface waters.

Detergent phosphates have been blamed for degrading fresh water lakes and there is no doubt that several lakes have been abused with phosphates and sewage. Sewage treatment will alleviate most of the problems associated with point-source loadings of lakes.

How much of an impact has detergent phosphate made on the fresh water contained in the lakes of the earth? Before considering specific examples it is informative to view the total picture. The grand total of all the phosphorus converted into detergents during the history of the industry is less than 2.2×10^{10} lb (about 10^{10} kg): less phosphorus than was mined in 1976. If all the detergents ever manufactured were instantaneously dumped into the lakes of the earth the concentration of phosphorus would rise by less than 80 parts in 10^9. During the 30 years during which phosphate detergents have been manufactured the fresh surface waters have cycled nine times and even if all the detergent phosphate had remained soluble the concentration would have risen by on average only 10 parts in 10^9. But because phosphates are poorly soluble in natural waters it is completely safe to state that detergent phosphates have raised the concentration of phosphorus in the lakes of the earth by no more than 10 parts in 10^{12} as a maximum limit!

Obviously, the problems associated with phosphates and lakes are not global and the detergent phosphate is not uniformly distributed in lakes. This is precisely my point: the problems are highly localized. It should also be noted that we have assumed that all the phosphate detergent was sewered to lakes; this is not the case. At a maximum, no more than 20% of the total phosphate from detergents is received by lakes. Most of the detergent phosphate is sewered to rivers which rapidly flush it to the oceans which are already saturated with phosphates.

Fig. 4 represents the major natural cycle of phosphorus. The phosphorus is delivered to the land masses when they are inundated by the seas and then fresh water returns the phosphorus to the seas after they recede. Fig. 5 shows the major contribution of mankind to the cycle.

In 1966 the phosphate rock industry mined 8.49×10^6 tons of phosphorus as rock. Where is this phosphorus in 1977? The fertilizer industry produced 7.87×10^6 tons of phosphorus as fertilizer during the 1966–1967 seasons. All other uses of phosphorus took the remaining 620 000 tons. Of this, 557 000 tons were converted into detergent phosphates; food supplements, toothpaste *etc.* consumed the remaining 63 000 tons.

I shall make the following assumptions:
(1) of the fertilizer added to the soil, 10% of the phosphorus was removed by cropping in the first year, 7% in the second year, 5% the third year, and 3% in each subsequent year;
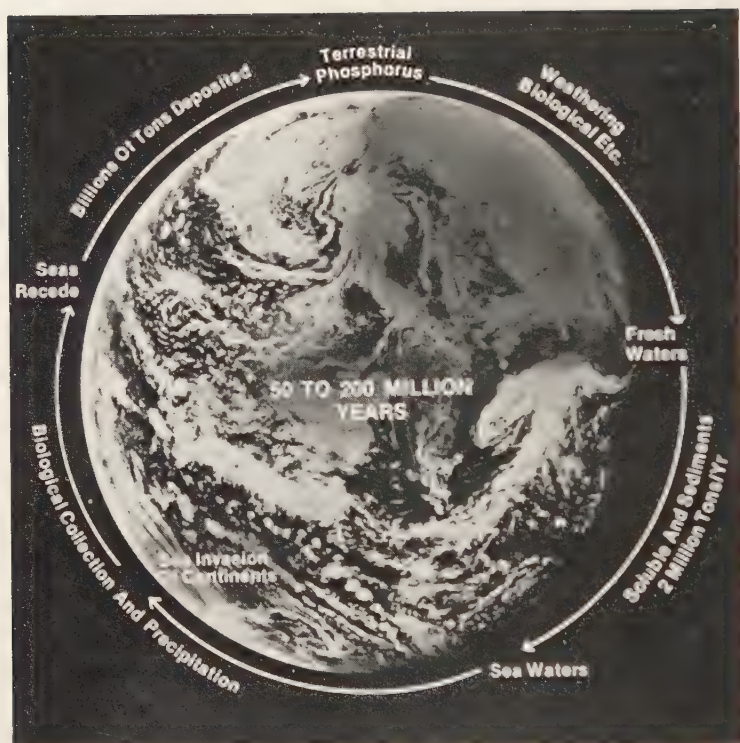
FIG. 4. The major natural cycle of phosphorus.

(2) the phosphorus was added to soil at the rate of 16 ton/mile^2 (6.8 t/km^2) and the wind and rain erode 250 lb mile^{-2} yr^{-1} (44 kg km^{-2} yr^{-1}) or about 1.25 ton/mile^1 (0.53 t/km^2) in 10 years;

(3) 10% of detergent phosphate is sewered to lakes, 60% to rivers and 30% to septic tanks.

After 10 years, at least 99.9% of the phosphorus mined in 1966 will no longer be in solution and about half was never dissolved during the 10-year period but was transported as a solid, if it moved from where it was applied.

The 1966 fertilizer should treat 490 000 mile^2 (12.9 × 10^5 km^2) of farm land. After 10 years, 3.38 × 10^6 tons should be removed by cropping and 0.613 × 10^6 tons lost by erosion, leaving 3.88 × 10^6 tons as insolubilized phosphorus on the land to which it was applied 10 years ago; that is, about 50% has entered the water system either as food, dissolved phosphates or silts. Whether the phosphate in the run-off waters from a farm enters a lake or a river will depend on the relative size of the drainage basins of rivers and lakes in the
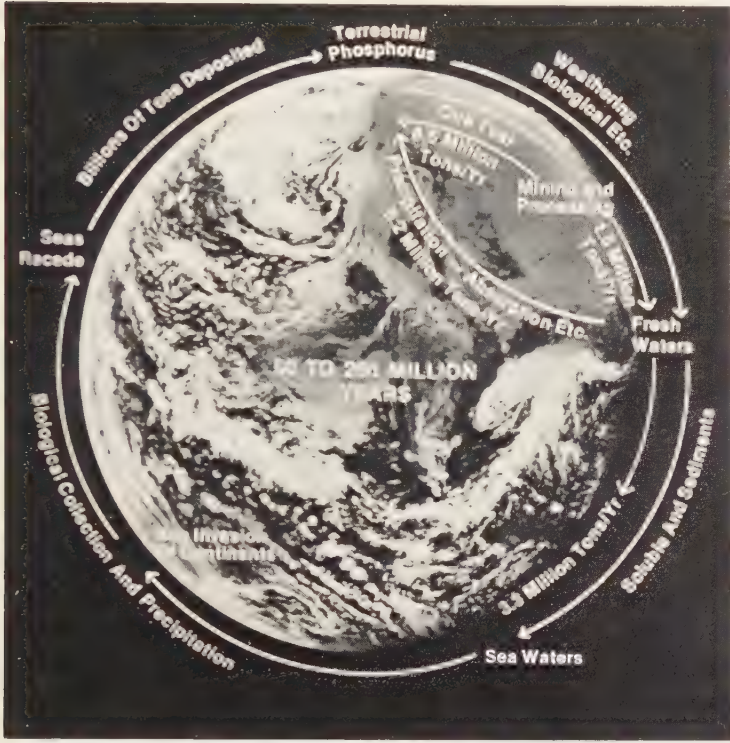
FIG. 5. Mankind's influence on the major natural cycle of phosphorus.

farming areas of the world. At least 90% of the drainage basins flows into the seas without entering a lake. I assumed that 0.613×10^5 tons of run-off phosphorus entered lakes but this is probably a high value for most areas of the earth.

Of the 3.38×10^6 tons which were removed by cropping, some was returned to the soil as animal and plant waste. I assume that two-thirds was returned to the soil and one-third was incorporated into food after the 10 or more small farm cycles were completed. The 1.13×10^6 tons in pet and human food are divided by the method used to sewer waste. The 30% deposited in septic tanks or similar land areas will remain in the soil for all practical reasons. The 60% sewered to rivers will be in the ocean or in the landfills of the sewage-treatment plant. If 20% of the phosphate sewered toward lakes is removed by treatment, then 9.0×10^4 tons should reach the waters of lakes. On average at least 90% of the phosphorus should precipitate into the sediments of the lakes and 9.0×10^3 tons should join the phosphate in the rivers moving to the oceans.

Detergent phosphates must be handled exactly as food phosphates because they are sewered in the same way. About 167 000 tons of phosphorus will be sewered to septic tanks and will become landlocked while 334 000 tons will reach rivers or sewage landfills. About 4.5×10^4 tons should be received by lakes, of which 4×10^4 tons should precipitate into the sediments.

In summary, of the 8.49×10^6 tons of phosphorus mined in 1966 about 84% should be landlocked, about 13.7% should be in ocean sediments, and about 2.3% should be in lake sediments by 1977.

As each person passes about 1 g of phosphorus each day as waste, the earth's 3.357×10^9 inhabitants passed about 1.35×10^6 tons of phosphorus in 1966. From our estimates about 25% of the food ingested by humans in 1966 was derived from the fertilizer added in the 1965–66 growing seasons. This highlights the reason why mankind has no other choice than to mine phosphorus if he is to eat. It also highlights the large quantity of phosphorus ingested by humans.

POINT SOURCES AND INTEGRAL SOURCE LOADINGS

As the term implies, a point source of phosphorus on a lake is any source which feeds phosphorus into the lake at a single point; it may be an industrial waste or a sewage pipe. An integral source is one that includes the integrated area of the watershed feeding a lake.

In densely populated regions point-source loadings of phosphorus are usually greater than integral loadings. Fortunately, this fact allows for remedial actions at several isolated points rather than requiring alterations of the general watershed to a lake.

Lakes are poorly structured to cope with waste effluents and whenever possible waste should not be routed to lakes. But it has been demonstrated in Europe and the USA that some smaller lakes can tolerate properly treated sewage, within limits. As the population continues to increase even this approach may prove to be inadequate.

The best immediately-available method of protecting lakes from overproduction in populated regions is proper sewage treatment. Whether or not man can find satisfactory replacements for detergent phosphates will not alter the requirements significantly. Phosphorus from other sources will quickly overtake and exceed acceptable limits in lakes subject to overproduction if adequate sewage treatment is not provided. Lake Erie is a prime example and has been the focal point of the phosphate issue in the USA.

To reduce the point-source effluents flowing into Lake Erie the State of New York and the Canadian Government prohibited the use of detergents

containing phosphate builders. The detergent manufacturers reduced the quantity of detergent phosphates sold in the Erie Basin area by more than one-half. Strict laws were enforced to prohibit industries from disposing of waste phosphates into the lake and the number of sewage-treatment plants removing phosphates has been increasing yearly. Today the total loading of phosphorus to Lake Erie is less than 51% of the loading in 1966 while the municipal loading has decreased to 35% of the 1966 value.

The time is rapidly approaching when point-source loading of Lake Erie will have reached a minimum limit but integral loadings still remain near the 1966 value of 15 000 kg/day. The time is also rapidly approaching when a definitive answer to the prime question can be obtained: has the removal of phosphates from the sewage entering Lake Erie significantly improved the water quality of this lake? The price has been great. It is to be hoped that there will consequently be a dramatic reduction in the number of algae in this lake.

SUMMARY AND CONCLUSIONS

Mankind has had almost no influence on the giant natural cycles of phosphorus. Natural transport has carried thousands of times more phosphorus than the transport induced by man.

Most of the phosphorus mined by man as an insoluble apatite returns to an insoluble apatite in a short period and most of the phosphate remains land-locked as it was before it was mined.

Man must have phosphate fertilizers because he cannot feed himself without them. As much as one quarter of the food on the earth is generated by the phosphate fertilizer applied in the year the food is harvested.

There is no worldwide phosphate problem of any kind. The supply is adequate for hundreds of years and there is no reason for a shortage ever to occur. The problem which exists with phosphate-induced overproduction in lakes afflicts only a small fraction of the lakes, usually in areas with high population densities. As has been known for several years removal of phosphates can effectively control overproduction in phosphate-limited lakes. Whether or not similar treatment of large lakes such as Lake Erie will yield the desired results is not yet known but the answer is pending.

Phosphates are one of man's most wonderful possessions. They rank in importance with clean air and pure water and they should be cherished rather than maligned. Yet the general public of the USA has learned to consider phosphates as an enemy of mankind: phosphorus, an evil element. It is our duty to inform the public that phosphates are not poisonous, that phosphorus is a friend of mankind and that, without phosphorus, we have no food.

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Discussion

R. J. P. Williams: I want to discuss now Dr Griffith's comments about phosphorus in the life system and postpone discussion of the detergent issue until other papers on that subject have been given (see later in this volume).

Inch: How easily is phosphorus in the form of phosphate leached from soils into the water supply?

Griffith: It depends on the soil. Phosphate is easily leached out from fertilizers added to a sandy soil but only with difficulty from those added to a clay soil. In a recent study on septic tanks Jones & Lee (1977) concluded that even in sandy soils phosphorus would probably move no more than about 3 m (about 10 ft) away from the septic tank. Phosphorus in igneous rocks needs a long time before it is degraded and able to be removed.

Inch: Presumably the leachability of phosphate also depends on the metal content of the soil and so on. This relates to Dr Loughman's comment (p. 65) about the soil accumulating phosphate from fertilizers and how much is releasable for vegetation.

Griffith: Mattingly & Talibudeen (1967) report that 100 years after phosphate fertilizers were applied to soil one can still detect significant benefits from them. It is a matter of kinetics: how much is one trying to grow in what period of time?

Pirie: Archaeologists can recognize old farming sites from their phosphate enrichment dating back tens of thousands of years (see, e.g., Mattingly &

Williams 1962; Clark 1976; Eidt 1977). Obviously phosphorus is not available as phosphate otherwise plants and animals would have removed it.

Larsen: The idea of a soil 'bank' in which phosphate remains until it is drawn on in time of need is wrong. Phosphate could not possibly stay at such a high level of chemical or biological availability. Its availability must decrease with the passage of time (Larsen *et al.* 1965).

Loughman: I considered the 'bank' over the short-term. After all, the soil is in equilibrium; if phosphate is bound, it must be in equilibrium with the low concentration in the soil solution.

Tinker: Dr Griffith put his finger on the problem when he said that it is a matter of kinetics. The phosphate is still in the soil and, without a doubt, one can detect phosphate applied up to 100 years ago on the old plots at Rothamsted and elsewhere, where no extra phosphate has been applied for 50 years. The crucial question is, how fast can the plant get it out? Crop growth is a rate process, and there is only one short growing season for most crops. For a good yield, phosphorus has to be supplied at a rate of about 0.3-0.4 kg d^{-1} ha^{-1}. Are the availability (which I define as the solution concentration of phosphorus in the soil) and the diffusivity of the phosphate in that soil such that the root system of the crop being grown can absorb at that rate?

With regard to phosphorus cycling, it is clear from Dr Griffith's figures that most of it is not cycling at all; it is going from rock to soil and staying there. The central question seems to me to be how to complete the cycle more efficiently?

How do we design root systems and crops that can extract phosphorus at the rate needed for maximum growth from soils that contain a low phosphate concentration? If we have to raise the phosphate potential too high to get maximum growth, then we get losses of phosphate due to leaching, slow chemical changes, erosion and so on.

Shaw: Can microorganisms be manipulated so as to make the phosphorus biochemically more available?

Tinker: That was discussed in detail at the symposium on *'The Role of Phosphorus in Agriculture'* at the National Fertilizer Development Center (Alabama) (1976). In my opinion none of the phosphate-solubilizing bacteria has been proven to have any significant effect. On the other hand, an efficient mycorrhizal symbiosis can extract phosphorus at a much faster rate than a non-mycorrhizal root system can from a given soil.

Loughman: Because it is redesigning the root.

Brydges: With regard to the soil bank of phosphate, when ground phosphate rock is added to soil, the phosphate becomes available to plants. Surely it dissolves until either it is all in solution or the availability falls off

owing to additional mechanisms, for example the particles being coated with iron oxide.

R. J. P. Williams: Grinding will make certain parts of the structure that are on the surface much more soluble because they are no longer in equilibrium with the bulk. The thermodynamic activity at the surface gives high solubility to a small amount of material. It is extremely likely that the remaining surface, a more regular crystalline form, has a lower solubility. But as the particle size decreases, the solubility increases again.

Griffith: Also, grinding changes the phase state of a substance; phosphates, in particular, tend to become amorphous. So small particles can have an amorphous coat, which is more soluble than the particle itself.

Brydges: If this were true, why was there such a burst of growth in the Cambrian period? After all, there was nobody to spread the phosphate around.

Griffith: For the same reason that underlies present-day growth in jungles.

McClellan: But the soils of modern jungles are characteristically very low in phosphorus.

van Wazer: Phosphorus is stored in plants in jungles, not in the soil.

Brydges: That means it is available for recycling to maintain growth and, most likely, that is what happened in Precambrian and post-Cambrian times.

McClellan: Despite the eminence of Dr Vincent McKelvey (director, US Geological Survey) in the field of phosphates, there are still half a dozen well known Precambrian phosphorites, including the material in Australia, India, USSR, the northern part of Michigan in the USA and in the Smoky Mountains (to name a few). So the argument about Cambrian or Precambrian (cf. p. 76) is rather academic.

With regard to the grinding of phosphate rocks, evidence does not substantiate any comment made here so far about an increase in solubility on grinding; sedimentary phosphorites are very porous with large surface areas and grinding does not affect their solubility.

R. J. P. Williams: So the form of the rock is not like a crystallite?

McClellan: These materials are microcrystalline. The characteristic particle size or crystallite size for a sedimentary phosphorite is about 40–60 nm. It is difficult to imagine a grinding process which can significantly alter that.

R. J. P. Williams: If that is true about the nature of the rock my statements are incorrect; I had assumed a bigger initial crystal particle size. So the answer to Dr Brydges' question is that once phosphate rock is put on the soil the particles should continue to dissolve.

McClellan: They do. The principal difference between the use of phosphate rock for direct application and the use of water-soluble phosphates

is that the solubility of the former (or its 'available phosphorus') apparently continues at the same level for a long time whereas water-soluble phosphates are available only for a short time.

Larsen: It has been said that phosphate in the natural environment (water, rocks etc.) is orthophosphate not polyphosphate (Landgreen 1954). According to one hypothesis, during the period when life on this planet began, hydroxyapatite acted as a catalyst to form diphosphate (or 'pyrophosphate') which with amino acids was instrumental in the creation of the first form of life (Miller & Parris 1964).

Griffith: I have just recently discussed abiotic polyphosphate formation (Griffith 1977) particularly with regard to the Precambrian era. Hydroxyapatite may have acted as a catalyst but that does not seem to be the necessary way to form the $P-O-P$ linkages in the environment. Reduction of iron(III) orthophosphate, for example, gives the pyrophosphate, which has the $P-O-P$ linkage. With this linkage as a phosphorylating agent it is not difficult to envisage spontaneous phosphorylation. The problem facing evolutionary chemists (such as Ponnamperuma, Gabel *et al.*) was, where did the phosphorus come from in the first place? As the apatites are almost insoluble, the primaeval broth must have had a relatively high percentage of phosphorus if amino acids were to have contributed to the spontaneous production of life. I am not even sure what hydroxyapatite is!

Loughman: Hydroxyapatite can be a biological product as in bones and teeth. If plant mitochondria are given high concentrations of phosphate and calcium, hydroxyapatite deposits inside them. We cannot separate simple chemical things from biological processes.

Pirie: When, 400–500 million years ago, calcium phosphate or hydroxyapatite forms appeared in bony structures, was that because the sea became saturated with phosphate? I ask because Mourant (1971) suggested that a virus infection started this burst of growth in many different phyla at almost the same date.

Griffith: Until the seas became saturated in phosphate about 500 million years before the Cambrian era (i.e. 3000 million years after the beginning of the lithosphere) there was a sufficient amount of free phosphorus to feed the life that was there. Algae existed before this time but the Trilobites and other, similar, organized forms of life seemed to come about in that period. Calcium phosphate appeared as a structural material in the post-Cambrian period.

R. J. P. Williams: Why should calcium phosphate have replaced the calcium carbonate which, presumably, was abundantly present?

Griffith: Until that time the oceans were dilute enough in phosphate to act as a sink. Once they became saturated, the more easily leachable and transferable phosphates were available.

R. J. P. Williams: Did calcium phosphate first appear as an exoskeleton or as an endoskeleton? An endoskeleton is easier to make because the constituents can always be concentrated.

Griffith: It is first found in an exoskeleton in Trilobites (i.e. during the early Cambrian period).

van Wazer: Our discussions about the phosphate 'bank' concept have so far dealt with the way that the phosphate is deposited. But the bank has various 'accounts' in two main categories: (1) phosphates in the various life forms (including soil microorganisms) and (2) soil phosphates not in living matter (which include some that is easily removable). Soil contains iron–aluminium phosphate colloids (which, being amorphous, are highly soluble), tiny crystals of apatite, phosphates sorbed on humus materials and other non-living forms. Phosphate is continually being exchanged between these accounts. The proportion in each depends on how the soil is handled, the condition of the soil, what was grown on it, what had previously been grown on it, and many other factors, all of which determine the amount of phosphate that can be withdrawn.

Larsen: During those exchanges the phosphate must be trapped in less reactive forms until finally it is stored as the crystalline form (even though that process might take a long time). As time passes, however, this adsorbed phosphate must finally be converted into some kind of crystalline phosphate (e.g. apatite).

van Wazer: I, too, believe in thermodynamics! But remember, the game of life is to beat thermodynamics; and life is one of the important account holders in this soil bank. The system is not controlled simply by inorganic thermodynamics.

Larsen: Compared with the amount of phosphate in the soils of industrialized countries, the amount in the biomass is only a small fraction. As Dr Tinker said, mycorrhizas act as an extension of the root system but I know of no evidence that they or any other microorganisms can mobilize phosphate which cannot be taken up by the plant.

R. J. P. Williams: Are there no bacteria that make their environment more acidic?

Larsen: The pH of the soil can be lowered only temporarily and locally (i.e. in pockets) because most soils have a tremendous buffer capacity.

van Wazer: How long does it take for the phosphate to be insolubilized? I imagined thousands of years but you seem to imply that it is just a matter of a few years.

Larsen: The half-life of the exponential decay of the availability varies from soil to soil (e.g. half a year in some Scottish soils to some 10 years elsewhere).

Pirie: The old technique of spreading rubbish, brushwood or straw over the soil and burning it, often called denshiring (derived from Devonshire), a standard practice in the late Middle Ages, was supposed to increase the fertility of the soil by making phosphate available (according to some people). Is it effective? If so, is that because it makes phosphorus available?

Larsen: It does work. Heat treatment of soil (with either dry heat or steam) can enhance the uptake by any crop three- or four-fold (Larsen 1966). But it does not mobilize phosphate. Thus the amount of available phosphate stays steady or decreases. Sterilization of the soil enhances root activity as there are no competitors.

Tinker: We have increased the growth of grass several-fold by γ-sterilization of soil, maybe as a result of this effect. But I would be surprised if mere burning of brushwood would raise the temperature of the soil sufficiently to have this effect. When stubble is burnt (a controversial issue at present) the temperature of the soil is not increased more than a few millimetres down. Only the heat from a burning forest would be sufficient to cause a significant sterilizing effect. The improvement from denshiring may simply be from the addition of ash which contains phosphate.

Kabbaj: If soil which is properly enriched with phosphate is supplied with an amount of phosphate corresponding to the uptake of the plants, what happens?

Larsen: To maintain the status quo one has to add more phosphate than the requirement of the crop to compensate for the loss due to chemical reactions in the soil.

Kabbaj: How much more?

Larsen: That depends on the soil. If the half-life of the enrichment with available phosphate is known, one can calculate how much more is needed. Generally speaking, a crop removes 10-20 kg P ha^{-1} and the soil needs a similar amount. That means one has to supply 20–40 kg P ha^{-1}.

Kabbaj: But that is not 10-fold as was suggested by the 10% availability of phosphate from rock. You are saying that 50% is available.

Larsen: Our figure was 43.2% (Larsen 1966) but on average for a well fertilized soil it is 10–20% although it can be as low as 5% in some soils.

Nicol: What happens to the remaining phosphate?

Larsen: It is accumulated in the soil. According to Cooke (1967) fertilizers have supplied nearly half as much phosphorus to British soils as is now present in the cultivated layer.

Harrison: In many upland soils, which tend to be poor and often not fertilized, burning of vegetation can also mobilize small but perhaps significant quantities of phosphate in the surface layers of the soil (Allen 1964;

Hansen 1969). [For further discussion of phosphate in soil, see pp. 287-291.]

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Phosphorus biochemistry

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Abstract   The biochemistry of phosphorus is outlined. As this element appears to have no redox reactions in biological systems phosphorus is always handled as phosphate and, as all phosphate compounds are thermodynamically unstable in water, phosphate uptake and incorporation are associated with energy consumption. The subsequent use of phosphate in metabolism and synthesis is illustrated by metabolic pathways and DNA (RNA) polymerizations, respectively. The importance and unique chemical significance of phosphorus in biology cannot be overestimated.

INTRODUCTION: PHOSPHORUS CHEMISTRY

Phosphorus has a diverse chemistry. It can exist in a range of oxidation states from -3 to $+5$ (PH_3 to P_2O_5) and can form relatively stable chemical bonds to a wide variety of elements. However the thermodynamic stability of the phosphorus compounds in water (see Fig. 1) is much more limited and this limitation restricts the biochemistry of phosphorus but not man's ability to interfere with its biochemistry. In fact the biochemistry may be restricted to virtually only compounds of phosphorus in combination with oxygen (i.e., in oxidation state $+5$) and all biochemical phosphorus compounds are then directly related to phosphate. In this case we should expect reactions of phosphorus to be limited to reaction (1).

$$[O_3P-OH]^{2-} + HO-R \rightarrow [O_3P-OR]^{2-} + H_2O \tag{1}$$
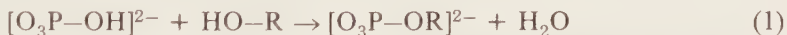
This proves to be close to reality. Overwhelmingly, phosphorus is used by life's reactions in a limited way. This very limitation provides an enormous opportunity for man to use his ingenuity and to introduce into living systems a diversity of non-biological phosphorus chemicals. For example, in so far as it is true that biochemistry is constrained to P—O and P—O—R systems, we can introduce a great variety of P—X compounds where X can be any element
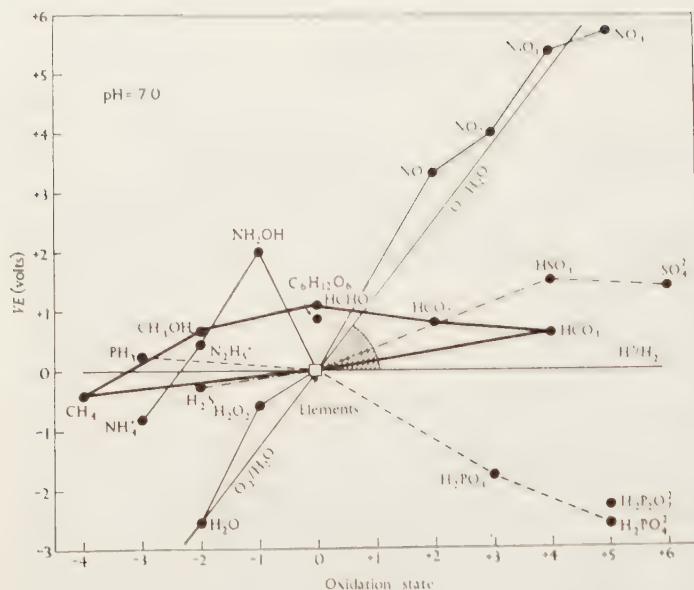
FIG. 1. An oxidation-state diagram for the non-metals (pH = 7) which shows the relative stabilities of the different oxidation states of the elements compared to the H_2/H^+ couple. The H_2/H^+ couple indicates the maximum thermodynamic reducing power available to biology. Elements such as I, N, S, C and Cl can be reduced but phosphorus (Si or B) cannot be (see Philips & Williams 1965).

such that P—X is not transformed immediately by water. Thus X can be H, B, C, N, F, Si, P, S, Cl but not Na, Mg, K or Ca. The deliberate introduction of P—X systems can be used and has been used in the chemistry of drugs, herbicides *etc.* but there is room for much further exploration. The accidental introduction of these compounds through industries unconnected with biochemistry produces pollution. Finally, we have the development of synthetic food-stuffs. Fertilizers are synthetic food-stuffs for plants and they are overwhelmingly phosphate compounds. Before looking at the ramifications of these general statements we must go back and look at the reason for the importance of phosphorus chemistry in biology itself.

PHOSPHORUS/WATER CHEMISTRY

Ionic equilibria

The main interest here is in the reactions of phosphate. Phosphoric acid, H_3PO_4, has pK_a values of 2, 7 and 12 and is a strong acid (cf. the pK_a values of carbonic acid, 6 and 10). Oxides of phosphorus cannot be used directly as

fertilizers and a choice of salt is open to man. The obvious choices of soluble phosphates are the Na^+, K^+ and NH_4^+ salts. Other reactions occur with phosphate at around pH 7. Phosphate forms relatively insoluble calcium salts and to a lesser degree magnesium salts. The equilibria of the soil are the same as those of cell biology and, just as calcium phosphate forms rocks on the earth's surface, so, by manipulating the intra- and extra-cellular concentrations of phosphate and of these cations, biological systems can make such materials as bone. [It is worth noting that, as the formation of bone requires energy, bone is a storage form of energy since blood is not supersaturated with calcium phosphate (see below)]. These are the major ionic reactions of phosphate.

The concentration of free phosphate in blood is around 1.0 mmol/l and as such it is bound, at least in part, as $[MgPO_4]^-$ and $[CaPO_4]^-$. The availability of phosphate from any solution is obviously controlled by several equilibria:

$$xM^{2+} + yPO_4^{3-} + wH^+ + zOH^- \leftrightarrows M_x(PO_4)_y(OH)_z(H)_w$$
$$\text{(soluble)}$$
$$\downarrow\uparrow$$
$$M_x(PO_4)_x(OH)_z(H)_w$$
$$\text{(insoluble)}$$
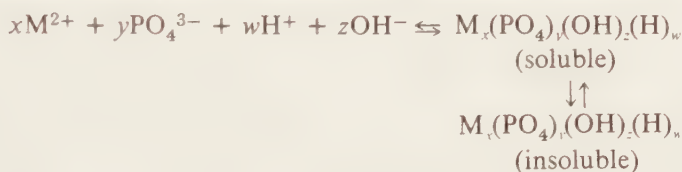
This set of reactions is not very different in the blood, in the soil, in plant sap or in cell cytoplasm. As part of our discussion will be about the *availability* of phosphorus to life processes these reactions are of great interest. Are all the reactions understood? Are they fast? Soil does not equilibrate rapidly with phosphate rocks. If we add phosphate in a soluble form to various life environments can it too be lost as an irreversible precipitate? Do we know the conditions of temperature, ionic strength *etc.* for the control of phosphate reactions with the metal ions? The problem is not just one of soil/plant relationships for it reappears in the incorrect deposition of phosphates in 'stones', in cataracts, in connective tissue and so on. One of the points at which man can exert an influence on the biochemistry of phosphate leads from a thorough understanding of these ionic equilibria.

The actual concentration of inorganic phosphate, $[P_i]$, in different biological compartments is important (Fig. 2). In external water (in soil) the concentration of free phosphate ($[P_i]_{out}$) is 1–10 μmol/l. In many cells it ($[P_i]_{in}$) is around 1 mmol/l. If we assume that the pH is the same in these two parts of space then energy, $RT \ln ([P_i]_{in}/[P_i]_{out})$, is consumed to force P_i up the concentration gradient. The biological system pumps in phosphate. Crossing different cell membranes (Fig. 2) involves different $[P_i]$ gradients and different energetics. In blood, for example, the $[P_i]$ is about 2 mmol/l, so that

		Cytoplasm		Vacuole
			b	
		Aquo II		Aquo III

Aquo I   a

		Cytoplasm		Chloroplast
			c	
		Aquo II		Aquo IV
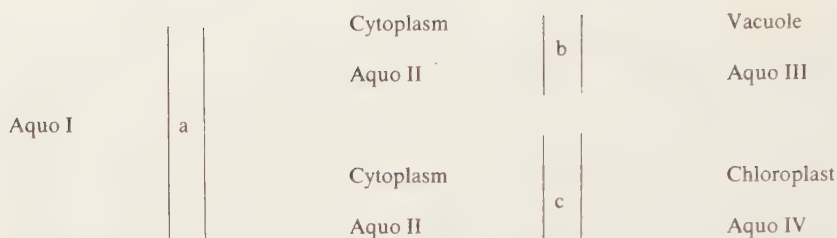
FIG. 2. The membranes a, b and c, which divide different aqueous compartments of a plant cell, are shown. Each compartment has its own particular phosphate concentration and each membrane may contain a phosphate pump.

the main concentration of phosphate in an animal is achieved before entry into most cells.

The uptake energy depends on the pH as well as the difference in concentration of inorganic phosphate. Low pH removes phosphate in a bound form (reaction 2).

$$H^+ + HPO_4^{2-} \leftrightharpoons H_2PO_4^- \tag{2}$$
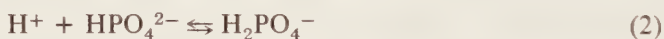
The more acid the outside medium, the more energy is expended in bringing phosphorus into a cell with pH 7. Thus ionic reactions can be used to pump phosphorus, e.g. with H^+ or metal ions. Chemical combination with organic centres also uses energy and traps phosphate (see later).

An aside to the state of the phosphate is worth noting. The best method for following phosphorus *in situ* is ^{31}P nuclear magnetic resonance (n.m.r.) spectroscopy. The method was used first by Moon & Richards (1973) and has been greatly extended since then (see, e.g., Daniels *et al.* 1974; Hoult *et al.* 1974; Henderson *et al.* 1974). The technique is now being applied to phosphorus in solids by the use of special pulse techniques and the use of 'magic angle spinning'. It is hoped to analyse for phosphate in free and bound forms not just in solutions in biology but in bone and other condensed phases, and the methods should be applicable to soils.

Bone formation. The formation and re-solution of mineral materials within a biological organism are controlled by cells. Thus there are cells which can build calcium phosphates against a concentration gradient and cells which can dissolve these phosphates by reducing the external phosphate concentration. The exact processes are not yet known but it is thought that silicon as a trace element is essential to the initiation of bone growth. The interaction and inter-relationship of silicon (and for that matter boron and possibly arsenic) and phosphorus have been poorly studied. Of great interest here is the material which is deposited out of solution, for it is not a simple crystalline calcium phosphate. As with other biological minerals it is the amorphous

state which life must form so that the continuous remodelling of the bone (and shell) can occur rapidly. The consequent solubility problems are not dissimilar from those which arise when various natural mineral phosphates are added to soils. It appears that much of the usable phosphate deposits on the earth's surface have been through a biological system once.

Hydrogen-bonding. Phosphate forms strong H-bonds to many basic centres. The most obvious is that to water, $P-O \cdots H-O-H$, and to soil silicates, but in proteins and elsewhere phosphate is often bound to the basic amino acids, lysine, arginine and histidine. Arginine is perhaps the most effective in that it forms a chelate:
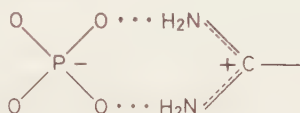
X-ray crystallographic studies on the binding of coenzymes containing phosphate show that these hydrogen-bonds are valuable contributing factors in catalyses of phosphate transfer.

Condensations

Reactions of phosphate with Y—OH to form anhydrides or esters are not spontaneous. The equilibrium constants for the formation of products follow the basicity of the Y—OH; for example, as in the following series:

$$Be-OP > B-OP > C-OP > N-OP$$
$$Al-OP > Si-OP > P-OP > S-OP$$

Stable   Unstable
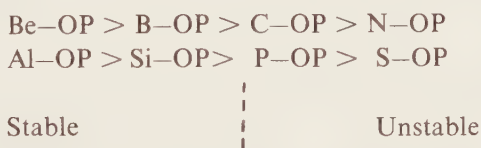
Despite the thermodynamic instability of even C—OP and P—OP these units are of outstanding biological importance, rating with the peptide bond. It is fascinating that the balance of the kinetic and thermodynamic stability of compounds of carbon and phosphorus in their highest oxidation states is similar. The similarity is shown in the order of hydrolysis energy of anhydrides (low stability) (> -42 kJ/mol) and esters (about -8.4 kJ/mol), and in the fact that condensates of COOH with H_2N (the peptide bond) are of roughly the same thermodynamic instability as that of phosphamides (e.g. histidine phosphate and creatine phosphate). Some biological polymers made by condensations are sugar—sugar compounds (saccharides), sugar—phosphate compounds (DNA, RNA, phospholipids), and amides

(proteins). I shall return to the kinetic control of the reactions of these unstable molecules (see below).

THE PHOSPHORUS REQUIREMENT OF BIOLOGY

Let us turn now to the main role of phosphorus in biology. The major building blocks of biology are covalent molecules, polymers, proteins, polysaccharides, RNA and DNA, and two types of phases discrete from aqueous phases—organic bilayer lipid membranes and salts. Of these RNA and DNA are polymers based on phosphate ester monomers (Fig. 3); the bilayer-lipid membranes are largely based on phospholipids (Fig. 4), and one of the salts is a calcium phosphate, bone. Phosphorus is then a bulk element in all life forms but is so to different degrees in different organisms. Phosphate compounds are involved directly in DNA and RNA but protein synthesis needs them too, in that it is the energy of a phosphate condensate, ATP, which drives the dehydration leading to peptide bond formation. Why has biology come to depend on phosphorus in so many respects?
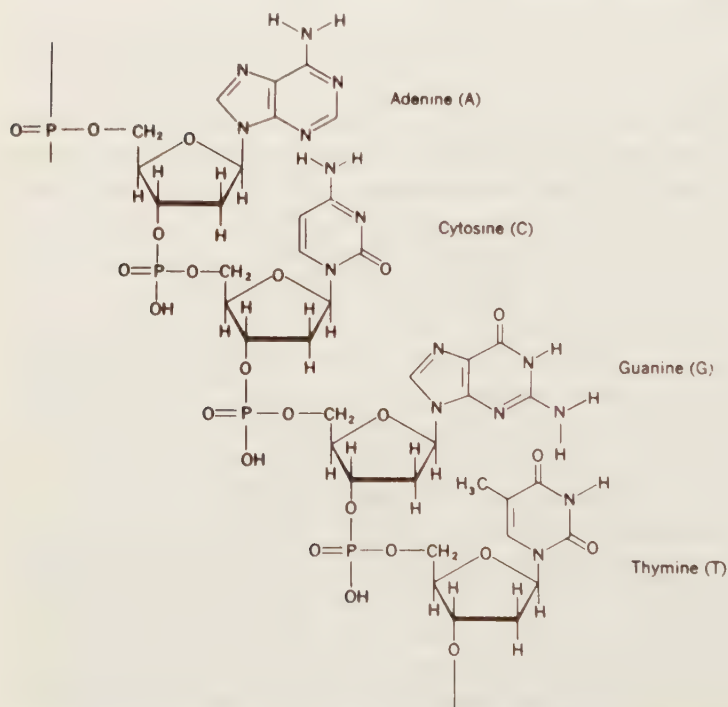
FIG. 3. An outline structure of DNA showing the phosphate ester groups. RNA is similar.
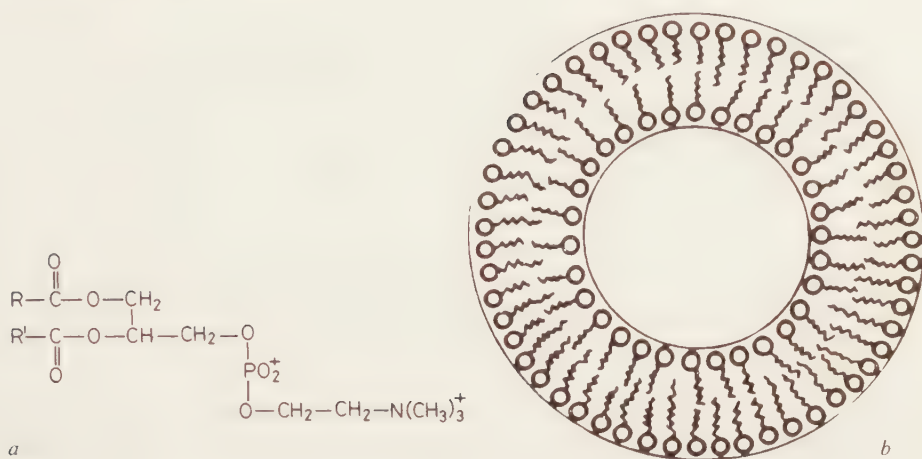
FIG. 4. The structure of a phospholipid lecithin (a), showing the way in which it forms a membrane (b).

The handling of phosphate and energy by biology

In as much as all phosphorus esters are unstable, the synthesis of all the phosphorus compounds needs energy. Phosphorus is not an element which can be incorporated into bio-molecules without energy in the same way as nitrogen from NH_3 or carbon from sugar or oxygen from O_2 can be introduced. Biological systems have found a method of handling energy and phosphorus which makes pyrophosphate its *earliest* chemical product (Fig. 5). In the use of photo-energy or of combustion energy or of the energy of sugar disproportionation (glycolysis), energy is transformed into an unstable bond, that of bound pyrophosphate in adenosine triphosphate, ATP, i.e. adenine—$P\sim P\sim P$, where $\sim$ represents a bond which is hydrolysed with the release of considerable free energy (reaction 3).

$$ATP \rightarrow ADP + P_i \qquad\qquad (\Delta G = + 42 \text{ kJ/mol}) \qquad (3)$$
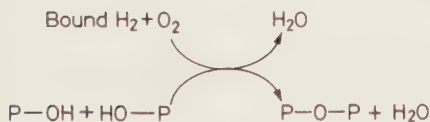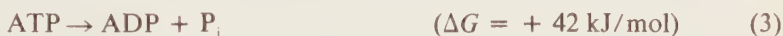
FIG. 5. The central role of phosphorus in life stems from the fact that the *initial* chemical bond used to transfer energy from light or redox reactions is that of pyrophosphate, P—O—P.

Phosphate entering biology is often handled along the path ADP + $P_i \rightarrow$ ATP and then ATP + XOH $\rightarrow$ XOP + ADP. The major source of ATP is the Krebs cycle (Fig. 6).

An alternative mode of incorporation is by reaction (4) which can be

$$P_i + \text{sugar} \rightarrow \text{sugar–P} \qquad\qquad (\Delta G = +\,8\text{–}12\,\text{kJ/mol} \quad (4)$$
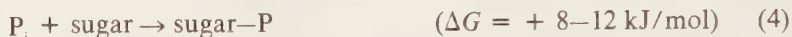
driven forward by metabolism (e.g. in glycolysis) of the sugar–P (a reaction which itself has negative ΔG). The pathway of glycolysis is one of interweaving ATP-driven and ATP-using reactions of sugar metabolism which synthesizes more molecules of ATP than it degrades.

The above passage stresses that the P$\sim$P bond is the usual energy currency of biology and that one energy-rich system can be used to drive another. Thus ATP can be used to form N–P bonds in histidine and creatine phosphates but these are rare synthetic steps. It can also be used to make any condensation polymer (e.g. protein) through the use of coupled reactions (5 and 6).

$$R^1NH_2 + HOOCR^2 \rightarrow R^1NH\text{–}COR^2 + H_2O \qquad (+\Delta G) \qquad (5)$$
$$H_2O + P\text{–}O\text{–}P \rightarrow 2\,P(OH) \qquad\qquad (-\Delta G) \qquad (6)$$
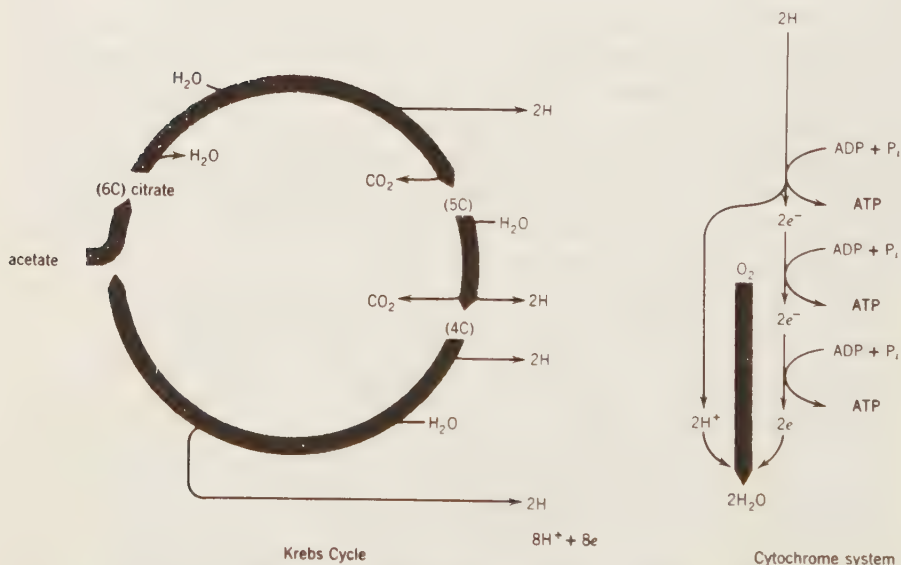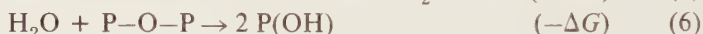
FIG. 6. The Krebs cycle showing the way oxidation of acetate is coupled to the production of pyrophosphate bonds in ATP, through the $4H + O_2$ reaction of Fig. 5 (see right-hand side of this Fig.: cytochrome system).

It is an unusual bio-polymer which is not made in this way. Although phosphate forms linear polymers—even linear polyphosphate—it does not form cross-linked polymers. The striking situation in the Periodic Table of elements is then that for the higher oxidation states of the elements we have a picture related to the pK_a values of the acids (see before):
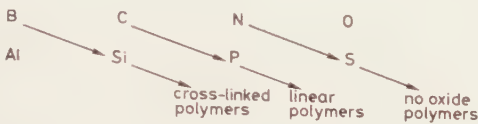
Carbon, phosphorus and nitrogen form the essential linear polymers of biological systems but phosphorus distributes energy in small pyrophosphates as well.

As a conclusion to this section I could list the huge dependence of biology on phosphorus but this would fill space without much purpose for this meeting. The major points we need to note are: (1) the gross requirement demands gross *availability* of phosphorus for maximum growth rates; (2) availability is not enough without energized uptake mechanisms; (3) uptake is followed by or occurs with incorporation; (4) interference in the pathways of phosphorus is possible; (5) the reactions need an energy supply.

The special role of ATP

Adenosine triphosphate, ATP, is at the centre of the energy transformations for chemical transfer (synthesis), uptake of chemicals across membranes and contractile mechanisms, and it can be used as a storage anion (e.g. in the chromaffin granules). The centre of interest of ATP is not only in its use (see Fig. 7) but also in its synthesis.

In some part this is still a mystery but increasingly it is believed that ATP is formed directly from charge separations within the special membranes of

FIG. 7. The central role of ATP in various cell activities is shown in the diagram. Charge separation occurs in the mitochondrial and chloroplast membranes and much of the resulting energy is then funnelled into ATP.

mitchondria and chloroplasts. This is indicated in Fig. 7 (Williams 1976; Mitchell 1977).

The concentrations of chemicals such as ATP then represent in some part the energy status of a cell for immediate action since we have:

$$\text{Energy stores} \leftrightharpoons \text{ATP} \rightarrow \text{Energy use}$$

The concentrations of ATP in various whole organs can be monitored, recently by n.m.r. spectroscropy, and its special significance is then seen. The concentration of ATP is often buffered by other energy-rich stores. The control concentrations of ATP are not managed just by thermodynamic equilibria but by the kinetic control of the break-down of pyrophosphate. Kinetic control is a further special feature in the reactions of phosphate in biology.

The kinetics of phosphorus chemistry

Phosphorus occupies its special position in biological systems through the fact that polymerization of phosphate is the link between redox energy and the chemical energy of hydration/dehydration reactions. The basic reaction of biochemistry is condensation polymerization. Of the elements of the Periodic Table we note that boron and silicon have oxides that are too basic and sulphur and nitrogen have oxides that are too acidic to allow them to engage in linear condensation polymers to the degree found in carbon and phosphorus chemistry. However, phosphorus and carbon chemistry differ in two important respects: (1) their redox chemistry and (2) the kinetics of reaction. Under (1) we have already seen that phosphorus is constrained to oxidation state $+5$ in biology but carbon can range from -4 to $+4$.

In so far as the kinetics of reaction are concerned, phosphate compounds are open to relatively rapid basic hydrolysis since S_N2 attack on the phosphorus centre is so easy. Thus, as well as being an extremely valuable control of the thermodynamics of biological systems, the bond $X-O-P$ is a valuable kinetic control in the transfer of fragments of either X or P. Typical examples are sulphate, sugar, amino-acid, base, and even sodium and calcium transfer. Phosphate binding often controls protein conformation.

The capture of phosphate in biology

The huge demand of living matter for phosphate is at the heart of the discussion in this conference. We must know what are the rate-limiting processes for growth with regard to phosphate since it is phosphate which life

receives, although it uses it in many different ways. I have already mentioned in passing one path of uptake in the formation of ATP. Consider an inner cell compartment where the reaction $ADP + P_i \rightarrow ATP$ is driven by light or oxidative metabolism (see Fig. 6). Clearly the reaction lowers the concentration of P_i so that P_i will diffuse into the cell from outside. Phosphorus is captured as bound phosphate. The mechanism for this uptake in photophosphorylation and oxidative phosphorylation has been described.

However, this is not the only method of phosphate transfer and we must look at how phosphate is moved into cells in plants and animals. This will be discussed later in the symposium.

Higher animals have a special problem, in that the growing young must have a phosphorus supply from the parent. In species which produce eggs the problem has been met by the use of a phosphate storage protein, phosvitin, which is made in the liver of the mother and stored in vesicles in the egg yolk. In some species the phosphate is mobilized from pre-existing stores in bone: milk too is rich in phosphorus. We must ask the question — can we as biologists improve these uptake mechanisms?

Substituting for phosphorus

For many reasons chemists and biologists may want to substitute another element for phosphorus. There is no substitute. The nearest element to phosphorus, arsenic, is poisonous. Even as arsenate it is an uncoupler of energy metabolism. Thus although there may be substitutes for some chemical elements (I doubt this myself) the situation in the case of phosphorus is clear-cut. (In passing, the use of arsenic in forced-feeding of cattle in the months just before slaughter has no explanation of which I am aware.)

The diversity of phosphates

The general incorporation of phosphate in the bases of DNA and RNA and the simple picture of membranes of Fig. 4 both hide the rich variety of compounds of phosphates in biology. The first extension I must note is the use of phosphate in the handling of many sugars. I have stressed that biology must do this so as to couple glycolysis with ATP formation. A different range of phosphates appear in lipid chemistry (Fig. 8). Lipids together with specific proteins give the individual membranes of one cell special properties (Table 1). Again membranes of different cells have different lipids in different membranes. We do not understand the reasons for the association of certain
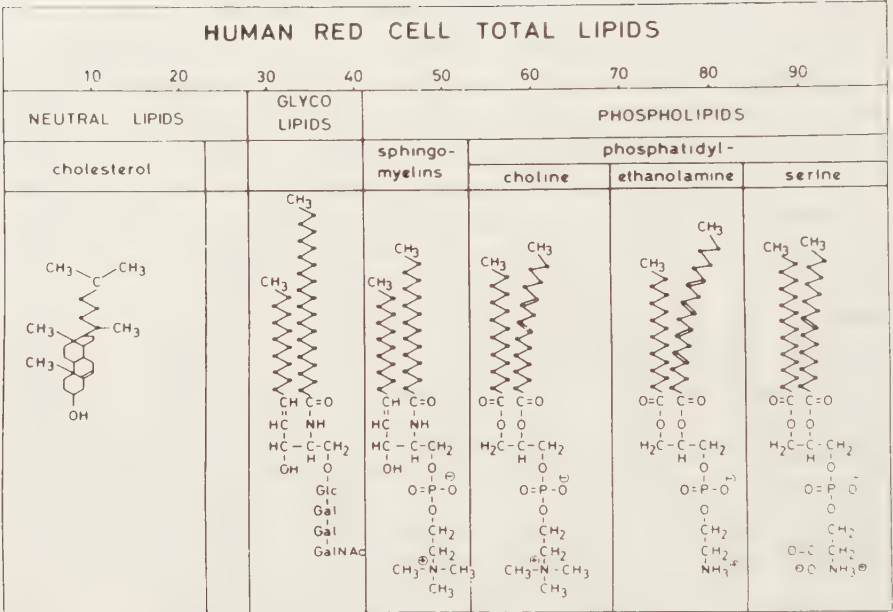
FIG. 8. The composition of the red-cell membrane showing the importance and diversity of the phospholipids.

TABLE 1

Differences in composition of phosphate compounds in different cell membranes from the same organism (man). The final column indicates the different rates at which different cells use ATP in membrane activity.

Fraction	Molar ratios		Ganglioside ($\mu mol/mg$ N)	Na^+,K^+-stimulated ATPase (μmol P split h^{-1} $[mg$ N]$^{-1}$)
	Cholesterol phospholipids	Cerebrosides phospholipids		
Cerebral membranes				
Myelin (large fragments)	1.03	0.5	0.07	36
Myelin (small fragments)	0.73	0.25	0.18	54
External synaptosome membrane	0.72	0.05	0.27	335
Synaptic vesicles	0.41	very low	0.07	0
Microsomes	0.48	0.09	0.14	163
Mitochondria	0.15	0.03	0.03	9
Other membranes				
Erythrocytes (plasma membrane)	1.17			
Intestine (brush borders)	1.11			
Liver (plasma membrane)	0.56			313

lipids with certain membranes nor do we understand how biology arranges the observed distribution of these compounds.

Phosphates also occur in wall polysaccharides and there they act as special binding centres for calcium and magnesium ions. Once again the full range of diversity and their functions are not fully known.

THE QUESTIONS

What I have described so far is the general biochemistry of phosphorus from which we see that phosphate could be rate-limiting for life given an adequate supply of other elements and energy for growth. This is common-place in agriculture. But do we know precisely the way in which phosphate is rate-limiting as far as plant (animal) growth is concerned in particular regions of the world? Is it in uptake, storage or metabolism? This may be more of a chemical than a biological question but we can next ask the biologists if it is possible to improve further the use of phosphate by the selective breeding of crops. There are two ways in which to improve yield: better growth on the same soils, and growth on artificially improved soils. We can ask the inor-ganic/physical chemists about the restrictions on phosphate uptake due to the interaction between soil and water. Finally, we can ask the organic chemists to help us by interfering in the metabolism.

Phosphorus drugs and herbicides

Just as there is a huge chemistry of carbon-based drugs there should be a huge chemistry of phosphorus-based drugs. In practice this does not seem to be the case although there are nerve-poisons, weed-killers, and even anti-tumour agents. The general principles are clear, however. We seek for P—O—X or P—X compounds which biology does not handle normally and which interact powerfully but specifically in biology. The rich variety of phosphorus compounds in biology suggests that there should be many ways of attack. The organic chemists will describe some of these later in the symposium.

References

I have given few references in this article as phosphorus biochemistry at the level I have described it here is to be found in advanced text-books of biochemistry. The first two references cover the biochemistry of phosphorus generally and are not referred to in the next.

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Discussion

Brydges: A problem often encountered when dealing with phosphate in aquatic systems is the variability of storage and uptake—the difference between what a plant or animal needs and what it will take up (if the phosphate is available). How do plants take up phosphate? Where do they store it?

Loughman: Phosphate not being actively used is stored in vacuoles. However, the total amount of phosphorus is meaningless from the point of view of the economy of the plant; what is important is the amount in the cytoplasm that can be used by the chloroplast or the mitochondria. Of the phosphate in an individual cell maybe only 1% or less participates in the sort of reaction Professor Williams was talking about because in many cases much of it is tied up, inactively, in the vacuoles. Phosphate may also be stored as polyphosphate granules, for instance, in some roots. Discrepancies have arisen because only recently has it been appreciated that only 1% may be active.

Brydges: Gross analyses of plant bodies show up to three-fold variations in total phosphate concentration but you are saying that the functional concentration may not change.

Loughman: Yes. When one compares a young cereal plant that may have only 120 µg P in the seed grown without phosphate for three weeks with another plant which has been raised on a high phosphate concentration (1 mmol/l), the latter plant may contain four times as much phosphorus at three weeks as the former. But when one measures the amount of ATP and other intermediates the differences between the two plants turn out to be relatively small. Nearly all the excess is inorganic orthophosphate, in the vacuole.

Griffith: The work of Menar & Jenkins (1970) on sewage-treatment plants in Texas at a time when many people were promoting the concept of 'luxury uptake' showed that the inorganic chemistry of phosphate dominated. On an increase in basicity (pH) of this system, the phosphates became much less soluble. Phosphate was adsorbed onto the sewage sludge as insoluble inorganic phosphate and was removed from sewage effluents in this way.

Reynolds: Some luxury uptake is observed among algae (see p. 204) but for no more than three or four cell divisions. In unicellular algae, which have no separate storage organs, 1% phosphorus (of dry weight) is about the maximum concentration found. There may be mechanisms by which the excessive products are excreted back into the medium which help the algae to regulate the cellular concentration of phosphorus.

Pirie: Professor Williams, why did you exclude phosphine? Marsh gas (will-o'the-wisp) contains phosphine. If it is not made biologically, how is it made? Is there not a biological reaction leading to the reduction of phosphorus(V)?

R. J. P. Williams: I cannot quarrel with the facts; if phosphine is found, that is that. First, let us consider the oxidation states of the common elements in biological systems (see Fig. 1 in my paper). For phosphorus, the states range from -3 (PH_3) to $+5$ (H_3PO_4). Fig. 1 shows the amount of energy that is needed to go from the $+5$ state to the -3 state per phosphorus atom, and similarly for carbon (from $+4$, CO_2 or HCO_3^-, to -4, CH_4). All the elements can be compared on such diagrams, and one can discover the maximum changes in chemical potential between the oxidation states of any element in anaerobic conditions. Take carbon, for instance; the carbon in sugar is at the same oxidation state as elemental carbon (i.e. zero) and the degradation of sugar to CO_2 and methane, CH_4, is simply an energy-generating disproportionation, a change from oxidation state zero to $+4$ and -4, respectively. Many carbon redox reactions can easily be driven in biology. For phosphorus, the amount of energy needed to drive phosphate to phosphine ($+5$ to -3) is much greater (see Fig. 1) than can be provided by the potentials found in biological systems. This does not mean that minute amounts of phosphine could not be produced. If the amount of phosphine present represents a partial pressure of 0.01 atmos, say, then there is a concentration factor of 10^2 in favour of phosphine production which does not enter into the oxidation-state diagram. The diagram applies to a standard state of unit pressure. So although minute amounts of phosphine might be made, a potential with such a slope as that for HPO_4/PH_3 cannot be reached, by a large margin, in any anaerobic biological reaction.

Pirie: And the phosphine is only there because, being a gas, it can escape?

R. J. P. Williams: Yes, at a very low pressure. (Although I don't know where the phosphine comes from!) Of course, methane or any of the biological reduction products could react outside the biological system on a rock surface, for instance, where there could be another non-biological chemical reaction, which could be coupled to supply the necessary energy to produce phosphine.

Shaw: But would that imply a reduction at some stage of the oxidation state of phosphorus from $+5$ to $+3$? Phosphorous acid $(HO)_3P_2$ will in some circumstances disproportionate into phosphoric acid and phosphine.

R. J. P. Williams: The slope is almost constant for the oxidation states of phosphorus (see Fig. 1) although it differs slightly at different pH values. Thus it is as hard to make phosphorous acid from phosphate as it is to make phosphine. But you are correct in that phosphorous acid can disproportionate.

In biology all these reduced states are liable to be oxidized anyway. Compare the H_3PO_4/PH_3 slope with that of O_2/H_2O. With oxygen present, phosphine would immediately be driven to higher oxidation-state compounds. It is the difference in slope of the two reactions that is the driving potential for any reaction.

Biological reactions can produce arsine (AsH_3), however, because arsenic is much easier to reduce than phosphorus (see Fig. 1).

Pirie: Why does nature use phosphate rather than sulphate esters? What is it that PO_4^{3-} will do that other anions will not?

R. J. P. Williams: To answer that, let me first make some general remarks. An overlooked feature of the Periodic Table is the diagonal relationship between the elements:

$$\begin{array}{cccc} Be & B & C & N \\ \searrow & \searrow & \searrow\searrow \\ Al & Si & P & S \end{array}$$
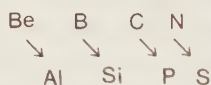
The inorganic chemist classifies more basic materials such as oxides separately from the strongly acidic materials. Beryllium and aluminum oxides are rather basic; boric and silicic acids are very weakly acidic; carbonic and phosphoric acids are somewhat stronger acids; and nitric and sulphuric acids are strong acids. The weakest acids, those of B and Si, condense most readily and form stable cross-linked networks. From the diagonal relationship it is clear that both carbon and phosphorus have the necessary acid-dissociation constants to participate in somewhat less-stable *linear* condensations, unlike most other elements. In contrast, the condensates of the strong acids are very unstable. For example, the energy for the condensation of sulphate into pyrosulphate

$$2 \ \overset{O}{\underset{O}{\overset{\diagdown}{\underset{\diagup}{S}}}}\overset{O^-}{\underset{O^-}{\diagup}} \rightarrow O = \overset{O}{\underset{O^-}{\overset{\|}{\underset{\|}{S}}}} - O - \overset{O}{\underset{O^-}{\overset{\|}{\underset{\|}{S}}}} = O \tag{1}$$
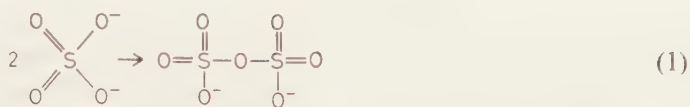
(reaction 1) is about $+125$ kJ/mol (cf. $+42$ kJ/mol for phosphate into pyrophosphate and <0.04 kJ/mol for silicate). Condensation of nitrate is even worse—almost impossible—and also the product would be a gas. In other words, sulphuric acid is too strong an acid and so gives no polymers, and aluminium is too strong a base and so gives very *stable* cross-linked condensates Al–O–Al at pH 7.

Biological polymers (e.g. DNA and proteins) are formed by condensations and these reactions must give linear products, not be of too great energy to proceed, and give only kinetically stable products. Carbon and phosphorus by virtue of their acidity constants can give such linear polymers. Silicon offers almost the same possibilities as phosphorus does, although (i) the esters of Si are energetically harder to form than the esters of phosphorus and (ii) silicate remains a weak acid after the first Si–O–Si link has been formed and so forms cross-links in two- and three-dimensional polymers. Thus carbon and phosphorus give especially important acids.

Pirie: But there are sulphate esters in biology.

R. J. P. Williams: They can be made, but at a greater cost in energy.

Loughman: Adenosine phosphosulphate (containing an adenine–P–O–P–O–S–O linkage) is the only way that sulphate can be activated for metabolic use.

R. J. P. Williams: Yes; the stability of the S–O–P group falls between that of P–O–P and S–O–S.

Inch: Carbon–sulphate esters are important in metabolism. Some processes depend on sulphate esters.

R. J. P. Williams: I agree; but the conversion of sulphate into pyrosulphate esters fails because the latter are all of too high energy. Only in a solvent such as $3\text{M-}H_2SO_4$ would formation of pyrosulphate be a reasonable possibility, where pyrosulphates might behave as polyphosphates do in neutral solutions.

Pirie: Some of the blood corpuscles of tunicates contain $4\text{M-}H_2SO_4$.

Larsen: As Professor Williams implied, biological formation of phosphine would be very significant from a geochemical point of view. Several groups have investigated the formation of phosphine in the laboratory (even with ^{32}P) but all have failed. There is no proof that phosphine is formed in any circumstances in any anaerobic system, be it natural or artificial (Hutchinson 1951).

Pirie: The spontaneously inflammable component of what is called phosphine is P_2H_4 not PH_3.

R. J. P. Williams: Whether P_2H_4 or PH_3, it would be detected if ^{32}P were used.

Pirie: But indubitably one sees a flash of light from these wills-o'the-wisp. What is the source of that light if it isn't the oxidation of some phosphorus compound?

Larsen: It is suggested to be an optical illusion. Farmers, however, claim that the self-ignition of wet hay is caused by a formation of inflammable gases during the decomposition of the hay.

Griffith: Those who speculate about the primitive earth during the period when a reducing atmosphere is hypothesized were encouraged when phosphine was detected in the Jovian atmosphere. However, this finding may have no relevance for earth because, when such an atmosphere might have prevailed, the phosphorus would have already been locked up in the silicates of the lithosphere. Since no natural silicides are found on earth, it seems completely improbable that silicon would have been oxidized while phosphorus coexisted in a reduced state. When the lithosphere solidified, phosphorus must have been in the $+5$ oxidation state.

R. J. P. Williams: Not necessarily; the slope of SiH_4/SiO_2 couple (see Fig. 1) is steeper than that of the PH_3/H_3PO_4, so silicon would be oxidized first.

Griffith: That is so, but silicon is the predominant member of the lithosphere whereas phosphorus is just a trace and I can hardly imagine how one could have been oxidized without the other.

R. J. P. Williams: Although life probably started in a reduced atmosphere, the reduction potential of the early earth is hard to know. At present we have oxygen in the air which at pH 7 is a highly oxidizing medium relative to hydrides of P or C. In the early reducing medium the slope of the H_2/H^+ potential was probably close to zero as shown in Fig. 1, and this could have been the redox potential of life systems. Note that this is similar to that for H_2S/S (see Fig. 1) and similar to that for CH_4/C. But even such potentials are inadequate for the formation of phosphines or silicides and I doubt their importance.

Griffith: Even if the atmosphere were reducing, there would have been a huge explosion as the system went through the explosive limits as the atmosphere passed from a reducing one to an oxidizing one. I can see no way to avoid that problem. At some stage lightning must have ignited the explosive mixture.

Pirie: Have you any reason to suppose that it did not?

Griffith: I don't have any evidence that it did!

R. J. P. Williams: Ammonia just needs a catalyst for oxygen to explode with it.

Labarre: As you said, in biochemistry phosphorus exists at the phosphate level. However, many anti-tumoural and neuroleptic drugs are injected into the human body with their phosphorus at the phosphine (-3) oxidation state. These phosphine derivatives are then transformed into phosphate groups which are inserted into DNA. But why do the phosphates corresponding to these phosphines have no effect on a disease such as cancer when they are injected? This surprises me because according to the oxidation-state diagram one should achieve better results by injecting the corresponding oxidized phosphate which should go to the right place. For example, one of the best anti-tumour drugs is tris(1-aziridinyl)phosphine sulphide, $(CH_2 \cdot CH_2 \cdot N)_3 PS$ (sold in France as thio-TEPA). The corresponding phosphate (P^V) has no effect.

R. J. P. Williams: I only discussed phosphate, as Drs Kirby and Inch will discuss organophosphorus compounds. However, when the oxidation state changes, the stereochemistry of phosphorus changes. As different drugs are often functional on the basis of their different stereochemistries, the answer to your question may be that phosphorus in phosphate is more or less tetrahedral and remains so throughout biochemical transformations.

Another important aspect is that the oxidation-state diagram describes the thermodynamics but the body works under kinetic control. The beauty of phosphorus and carbon is not just their favourable thermodynamics but also their favourable kinetics. When pyrophosphate is formed, it is relatively stable kinetically (although it is thermodynamically unstable). Therefore the movement of phosphate can be controlled by enzymes and so the location of the catalysts decides where the phosphorus compounds will be metabolized. The structural organization of the body controls the site of the phosphate reactions.

van Wazer: Another possible answer to Dr Labarre's question is that, just as arsenic acts as pseudo-phosphorus in many of its biological reactions, so this phosphine may be acting as a pseudo-ammonia.

R. J. P. Williams: Curiously, though, in biological systems arsenate does not work like phosphate: it completely uncouples the energy system.

van Wazer: That is because the activation energies for the reactions of arsenate are much lower and so the As–O–As and As–O–P linkages are extremely rapidly hydrolysed as soon as they are formed. That means that when an arsenate group is built into, say, an ATP structure, the product immediately falls apart. Thus the energy system is 'uncoupled' owing to the substitution of arsenic for phosphorus.

PHOSPHORUS IN SOIL

R. J. P. Williams: I am still not clear about the form organic phosphorus takes in the soil. A chemist sharply distinguishes inorganic phosphate from organic esters and compounds with carbon–phosphorus bonds. Only some organic phosphate is made available as inorganic phosphate on treatment of soils (e.g. with acid for phosphate esters) so that we need to know how much phosphorus exists in any one given soil as esters before we can consider ways of making it available.

Tinker: This can be determined. For example, a particular soil from Scotland contained about 60% P in organic combination and 30% of P is in inorganic combination. By suitable choice of soil one can find almost any ratio. To deal with this complexity, one has to go through a traumatic change from being a pure chemist to a soil chemist; there are so many different chemical species that one has to forget pure compounds!

R. J. P. Williams: But may we at least say that they are esters?

Tinker: All the phosphate is bound by orthophosphate ester links. No compound with a C–P bond has been found in soil, as far as I know. Sufficient maltreatment of the soil will gradually break the phosphorus in organic matter down into orthophosphate ions.

Kirby: How do you distinguish organic from inorganic phosphate?

Larsen: In the most common method the inorganic phosphorus is extracted with acid. (Chelating agents have been similarly used with reasonable results.) The distinction is acid solubility—but there is no clear demarcation line between the two. Some labile organic phosphorus may be hydrolysed during the extraction but quantitatively that is an insignificant amount compared to the bulk of the phosphorus in the soil.

Kirby: Could there be a substantial amount of inorganic phosphate in the organic fraction which was not detected as such?

Loughman: A calcium phosphate gel with protein adsorbed onto it, for example, might look like associated organic material. I suspect that a large proportion of this so-called organic material is inorganic orthophosphate. Some plants exclude inorganic ions such as zinc from their tissues (e.g. plants that adapt themselves to life on lead-mine tailings). The metal ion is bound in the wall and one would imagine that the membranes have great cation-exchange capacity because the wall contains a lot of galacturonic acid—that is how calcium is bound. Zinc, however, is not bound in this way because to remove it one has to treat the wall with cellulase and some other glucanases.

R. J. P. Williams: High-resolution solid-state ^{31}P nuclear magnetic resonance spectroscopy could be used to distinguish phosphate ester from inor-

ganic phosphate in soil material. Modern pulse and fast-spinning-sample techniques could be tried.

van Wazer: But even with the best special pulsing programme the lines are still too broad (about 50 Hz) to give much detailed information; furthermore, transition metals will cause much more broadening.

R. J. P. Williams: No. Schaeffer (Monsanto) has done some excellent ^{13}C n.m.r. work on solid polymers, observing sharp lines. In my paper I referred to several groups which have applied ^{31}P n.m.r. to phosphorus in all sorts of circumstances.

Abbott: In the Laboratory of the UK Government Chemist, we use ^{31}P Fourier-transform n.m.r. spectroscopy to distinguish orthophosphate from long-chain phosphates added to food-stuffs. It is in routine use when needed.

Kirby: Would it help to know the ratio of organic to inorganic phosphate in average plant material? I assume that the soil ratio should not be greater than that, and that no more organic phosphate is made after the plant dies.

Tinker: No, you cannot assume either of those things. Turnover is continual, owing to microbial metabolism.

Pirie: One would expect the amount of phosphate to increase because some microbial phosphorus compounds are extremely resistant and should build up an intractable mass.

Shaw: Could photoelectron spectroscopy be used to detect any difference between a phosphate ion and a phosphorus ester?

R. J. P. Williams: ^{31}P n.m.r. spectroscopy should be a sufficiently powerful tool; it can be used on less than 1 mmol/l P in solution and soon may be applicable to 1.0 mmol/l in the solid state. Many of the compounds which we want to investigate are more concentrated than that in both the solid and solution phases. For example, Navon *et al.* (1977) simultaneously differentiated the phosphorus in ATP, ADP, glucose phosphate and other phosphates in *E. coli* cells (for a general reference see Dwek *et al.* 1977).

Tinker: This sounds like a most exciting possibility. As far as I know nobody has used ^{31}P n.m.r. on soil phosphate but Goodman & Cheshire (1976) used electron paramagnetic resonance to identify copper porphyrins in soil organic matter. Could ^{31}P n.m.r. distinguish all the various phosphate esters which will be present, those in the phytins and so on?

R. J. P. Williams: I don't know; that is a matter for experiment. ^{31}P n.m.r. has been applied to some plant materials (although then the phosphorus was in solution) and solid-state materials.

Labarre: Now that it is agreed that organic phosphate in the soil consists of the PO_4^{3-} ion with many different organic ligands, one might extrapolate our knowledge of the behaviour of phosphate in the human body to develop ways

of activating it in the soil. In the human body enzymes will make available water-soluble phosphate from organic forms. These enzymes are metallo-enzymes. This seems to be one of the main roles of trace elements in the human body; for instance, with less than 1 part in 10^9 of copper we could not live. The phosphatases only work when the enzyme protein is activated by metal ion. It might be that the enzymes in the soil are not activated and that the spreading of a few g/ha of a specific metal might activate the enzymes to mobilize the phosphate from the organic phosphates.

R. J. P. Williams: Only some phosphate reactions which are catalysed by enzymes depend on metals. For instance, alkaline phosphatase is a zinc enzyme in *E. coli* and humans. Most of the other phosphate-transferring systems depend on magnesium but not on trace metals. I don't know about the acid phosphatases or whether the soil phosphatases, acid or alkaline phosphatases, need metals. If they are acid phosphatases, I suspect that they do not depend on trace metals. The enzymes that handle pyrophosphate nearly always depend on magnesium, sometimes calcium.

Harrison: By studying pH curves, we have been able to distinguish three types of soil phosphatases: alkaline, neutral and acid. Although all three may be present in neutral soils, usually only one or two forms are present in the same soil.

Loughman: Alkaline phosphatases in the roots of higher plants are zinc enzymes.

R. J. P. Williams [note added in proof]: I see I failed to mention the use of phosphorylation of proteins in control reactions. There seem to be many cases of the switching on or switching off of biological reactions by formation of serine or histidine phosphate bonds. This is an ideal control since these bonds are of low thermodynamic stability and hence their hydrolysis reaction provides a kinetic control of protein conformation.

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The organic chemistry of phosphate transfer

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Abstract   Studies in simple systems have identified the reaction mechanisms likely to be involved in biological phosphate transfer and provide the background for understanding the reaction *in vivo*. Metabolic pathways start from inorganic phosphate, but the introduction of organophosphorus compounds allows us to by-pass early steps and modify specific enzyme-catalysed reactions. In some cases, as with the nerve poisons, the effects are not specific to enzymes catalysing reactions of organophosphorus compounds. But the success of any rational chemical intervention depends on both our understanding of the biochemical reaction and the current state of synthetic organophosphorus chemistry.

The chemistry of the phosphate transfer process in cases where chemical intervention in metabolic processes has been successful is summarized, and some less familiar types of organophosphorus compound are discussed in the light of the apparent requirements for successful intervention.

Living systems do a great deal of organophosphorus chemistry, of which the most important reaction, by far, is phosphate transfer (reaction 1).

$$\begin{matrix} -O \\ >\!P \\ -O \end{matrix}\!\!<\!\!\begin{matrix} O \\ \\ X \end{matrix} + HY \rightleftharpoons \begin{matrix} -O \\ >\!P \\ -O \end{matrix}\!\!<\!\!\begin{matrix} O \\ \\ Y \end{matrix} + HX \qquad (1)$$
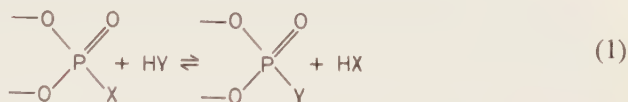
In practice nearly all organophosphorus compounds of biological or economic importance are phosphate esters or condensed phosphates, so the reaction most commonly involves transfer of the phosphate group to oxygen. An example is the ubiquitous kinase reaction (2).

$$\underset{\text{ATP}}{\text{AdO}-\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{P}}}-O-\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{P}}}-O-\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{P}}}-O^- + \text{ROH}} \underset{\text{enzyme}}{\overset{\text{kinase}}{\rightleftharpoons}} \underset{\text{ADP}}{\text{AdO}-\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{P}}}-O-\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{P}}}-O^-} + \text{RO}-\overset{O}{\overset{\|}{\underset{\underset{O^-}{|}}{P}}}-O^- \qquad (2)$$
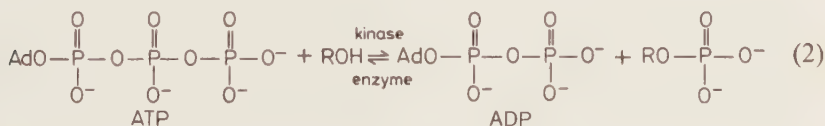
I shall discuss first the chemistry of the transfer of phosphate. The principles involved are the same for reaction in any conditions, but biochemical phosphate transfer is of special interest, not just for anthropocentric reasons, but because of the familiar but stimulating paradox that—thanks to catalysis by enzymes—the reaction is fastest in the mildest conditions.

The natural origin of the phosphorus found in living organisms is inorganic phosphate but with the enormous range of organophosphorus compounds now available—well over a million—it is possible to introduce phosphorus into biological systems in an enormous range of different forms. I shall concentrate on the two most important types of phosphorus compound, phosphate monoesters, and the fully esterified derivatives, e.g. (1).

$$\begin{array}{c}
RO \\
\diagdown O \\
 \diagup \\
P \\
RO \diagup \diagdown X \quad (1)
\end{array}$$
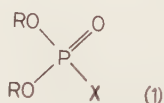
Structure (1) represents a typical laboratory phosphorylating agent, but many compounds of this type react with biological systems. Phosphate transfer from X to Y involves a two-step nucleophilic substitution by way of an addition intermediate (2).

$$Y^- \curvearrowright \underset{RO}{\overset{RO}{P}}\overset{O}{\underset{X}{}} \ \rightleftharpoons \ Y-\underset{RO}{\overset{O^-}{P}}\overset{}{\underset{OR}{X}} \ \rightleftharpoons \ \underset{Y}{\overset{O}{P}}\overset{}{\underset{OR}{OR}} \ + \ X-$$

$$\qquad\quad (1) \qquad\qquad\qquad (2)$$
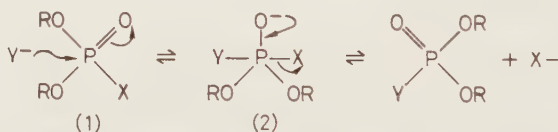
This mechanism is similar to that of acyl transfer by the corresponding carboxylic acid derivatives (3).

$$Y^- \ R-\overset{O}{\underset{X}{C}} \ \rightleftharpoons \ R-\overset{O^-}{\underset{Y}{C}}X \ \rightleftharpoons \ R-\overset{O}{\underset{Y}{C}} \ + \ X^-$$

$$\qquad\quad (3)$$
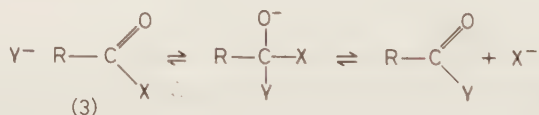
In particular, reactivity depends both on the reactivity of the nucleophile, Y^-, and on how good the leaving group X is. X can be halogen, in which case the compound (1) is a reactive acid halide, or oxygen, when reactivity can be controlled by a careful choice of the second substituent on oxygen (see Table 1).

TABLE 1

Reactivity of fully esterified phosphate derivatives, $(EtO)_2PO \cdot X$ and $(Pr^iO)_2PO \cdot F$, towards hydroxide ion, at 25 °C

X	Rate constant $(k_{OH} / l\,mol^{-1}\,min^{-1})$
OEt (poor leaving group)	5×10^{-4}
$O-\langle\ \rangle-NO_2$	1×10^{-4}
$O \cdot PO(OEt)_2$ (good leaving group)	160
$(Pr^iO)_2PO \cdot F$ (4)	50

TABLE 2

Relative reactivity towards nucleophiles of a phosphate triester[a] and the corresponding acetate ester[b]

Nucleophile	$k_{phosphate} / k_{acetate}$
F^-	50
H_2O	0.7
Acetate	0.4
HO^-	0.02
$NH_2 \cdot OH$	3.8×10^{-3}
Imidazole	2.9×10^{-3}
$NH_2 \cdot CH_2 \cdot COO^-$	1.2×10^{-3}
$NH_2 \cdot CH_2 \cdot COOEt$	4.7×10^{-4}
Pyridine	8.4×10^{-5}
4-Methylpyridine	4.3×10^{-5}

[a] Data for 2-(2,4-dinitrophenoxy)-2-oxo-1,3,2-dioxaphosphorinan (1; RR = $-[CH_2]_3-$, X = 2,4-$(NO_2)_2C_6H_3O$) from Khan & Kirby (1970).
[b] Data for 2,4-dinitrophenyl acetate (3; R = CH_3, X = 2,4-$(NO_2)_2C_6H_3O$) from Jencks & Gilchrist (1968).

This reactivity is important because a stable compound is of no use as a phosphorylating agent and too reactive a compound will attack the first thing it meets in a biological system, which will usually be water. Organophosphorus pesticides and chemical warfare agents are compounds of this type with moderately good leaving groups, based on oxygen or sulphur or sometimes fluorine. The well known strength of the P–F bond makes phosphorofluoridates (e.g. 4, see Table 1) considerably more stable than derivatives of other halogens, with reactivity comparable with that of the pyrophosphates. Reactivity also depends significantly on the nucleophile.

Fluoride, as might be expected, is a particularly good nucleophile for tetra-coordinate phosphorus (e.g. 1). Oxyanions are also reactive, rather more so than amines of the same basicity. This order of reactivity is very different from that observed for attack on the carbonyl group, and some representative data are shown in Table 2.

Biological transfer of phosphate involves less highly esterified derivatives of phosphoric acid. Removal of one esterifying group gives monoanions (5).

$$RO \diagdown \mkern-6mu \underset{\displaystyle \overset{\displaystyle P}{\diagup \mkern6mu \diagdown}}{} \mkern-10mu \diagup O$$

(5)
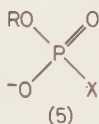
These are generally less reactive towards nucleophilic attack at phosphorus (often by a factor of about 10^3; Kirby & Younas 1970), but the reaction is qualitatively similar to that of the corresponding fully esterified derivatives (Khan & Kirby 1970). But the loss of both esterifying groups results in phosphate transfer of a quite different sort. Compounds (6) with poor leaving groups (e.g. X = OMe), which include nearly all the phosphate esters found in living systems, are stable at neutral pH, but reactivity depends strongly on the nature of X. Compounds with X = halogen are extremely reactive, with the predictable exception of phosphorofluoridate (X = F). But derivatives with oxyanion leaving groups vary widely in stability, from simple phosphate esters such as (7), which are stable indefinitely, to the unsymmetrical pyrophosphate (8), which has a half-life of 10 min at 35 °C (Miller & Ukena 1969).

(6) $\overset{\pm H^+}{\rightleftharpoons}$ (7)   (8)
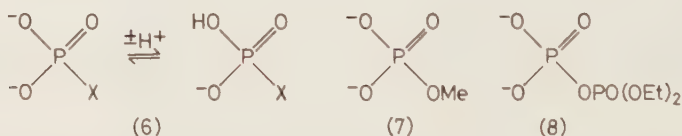
The phosphate group of a dianion is transferred to good neutral nucleophiles in a concerted displacement reaction (9).

(9)
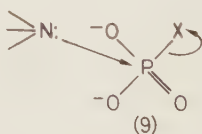
But the dianion is sufficiently electron-rich to expel a good leaving group without assistance, so that phosphate transfer to weak nucleophiles involves a two-step process through (10).

$$\begin{array}{ccc} {}^-O\diagdown\underset{\displaystyle \diagup\!\diagdown}{P}{}\!\diagup X & \xrightarrow[\text{slow}]{} & O^-\diagup\underset{\displaystyle \diagup\!\diagdown}{P} \\ {}^-O\diagup\quad\diagdown O & & O\diagup\quad\diagdown O \\ & (10) & \end{array} \xrightarrow[\text{fast}]{\text{ROH}} \begin{array}{c} RO\diagdown\underset{\displaystyle \diagup\!\diagdown}{P}{}\diagup O^- \\ O\diagup\quad\diagdown O^- \end{array}$$
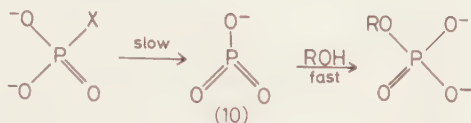
Here the slow step is a unimolecular reaction, in which the nucleophile plays no part. The rate, therefore, does not depend on the reactivity of the nucleophile. This is self-evident; but, remarkably, the same is true for the concerted displacement reaction (9): reactivity depends strongly on the nature of X, but little, if at all, on the nucleophile. Given a good leaving group X, therefore, the compound will transfer the phosphate group to any neutral nucleophile, whatever its basicity. This is an important advantage if the nucleophile is a weakly basic alcohol, ROH; particularly because anions like RO^- do not react with phosphate dianions, presumably because of electro-static repulsion (Kirby & Jencks 1965).

Biological transfers of phosphate presumably involve one of these basic mechanisms. The unimolecular pathway, through metaphosphate (10) could be important, but this mechanism seems to me to violate a basic principle of enzymology—that enzyme-catalysed reactions avoid pathways which involve high-energy intermediates. Furthermore, metaphosphate is an indiscriminate reagent (Kirby & Varvoglis 1967) and enzyme reactions are noted for their tight control at all stages. A graphic illustration of this point is the transition state (Fig. 1) for the transfer of phosphate catalysed by the enzyme creatine kinase, a picture which was built up from magnetic resonance spectroscopic experiments by McLaughlin et al. (1976). Here the phosphate group being transferred is fixed precisely by bonds to all five of the groups around P. The departing nitrogen atom is part of the bound creatine and the attacking oxygen atom is held in exactly the right position by the specific binding of the ADP molecule. All three of the negatively charged oxygen atoms of the group being transferred are involved in hydrogen bonds to the enzyme protein: one to the side-chain NH_3^+ group of a lysyl residue and the other two in a double hydrogen bond to the guadinium group of an arginyl residue.

It seems likely—on purely chemical grounds—that this type of picture will be general, that the nucleophile in an enzyme-catalysed phosphate transfer process will be in position from the beginning, and that such reactions will normally be concerted displacements:
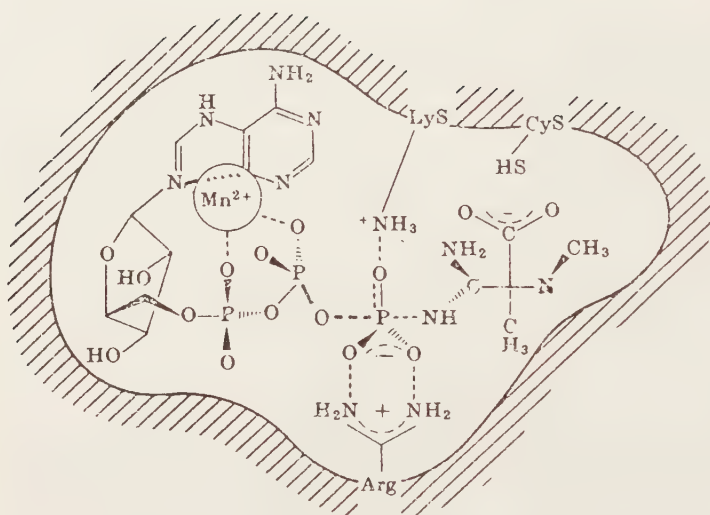
FIG. 1 Transition state for the transfer of phosphate catalysed by creatine on the right, ADP on the left, and by hydrogen bonds to lysine (Lys) and arginine (Arg) on the enzyme.
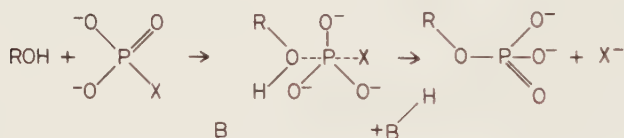
Overall the reaction amounts to a general base-catalysed displacement to give the dianion (11).

(11)
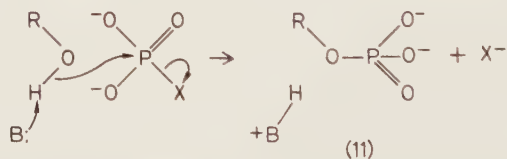
The complete mechanism has never been observed in a simple system, and it involves at least a partial negative charge on the nucleophile. But it is possible that the electrostatic barrier operates at distances of approach rather larger than those likely in an enzyme–substrate complex since the smaller barrier observed for the nucleophilic attack of anions on phosphate monoanions appears to be absent for intramolecular reactions (Bromilow *et al.* 1971).

I have said nothing so far about activation of the leaving group. It is not

difficult to see how the terminal phosphate of a pyrophosphate or a triphosphate like ATP might be activated, but phosphate groups are commonly transferred from simple alkyl phosphates, often initially to a hydroxy group of the enzyme involved, and in such cases the poor leaving group has somehow to be converted into a very good one.

The simplest way this can be done is implicit in the mechanism we have just seen (to give 11). In effect the problem is to reverse that reaction, which means protonating the leaving group, now RO.
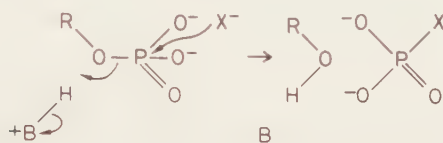
Complete proton transfer to the oxygen atom of the leaving group would make it an extremely good leaving group and is generally thought to account for the rapid hydrolysis of phosphate monoesters near pH 4.

A possible alternative is complexation with a metal. Bonding to a metal cation M^{2+} neutralizes the negative charges of the dianion, so that a mono-ester will come to behave more like a triester (12).

(12)
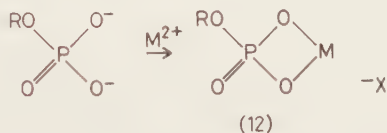
(Metal ions are often involved in enzyme-catalysed transfers of phosphate.) Neutralization of the dianion could help attack by a negatively charged species—though again there is no direct evidence—but it is important to realize that a triester is not necessarily more reactive than a monoester (Khan & Kirby 1970). The data in Table 3 illustrate this point: for the moderately good leaving group, nucleophiles of low basicity react faster with monoesters than with triesters.

For successful chemical intervention in a biochemical process one wants ideally to interfere with an enzyme-catalysed reaction. Enzymes operate at low concentrations, with high turnover rates, so that only small amounts of an effective chemical inhibitor are required. This has obvious economic advantages, when, for example, the target is a widespread population of insects. And only low concentrations may be practical in any case, because of the physical problems of access to the biochemical machinery involved.

TABLE 3

Relative reactivity towards nucleophiles of phosphate monoesters and triesters[a]

Nucleophile	$k_{triester} / k_{monoester}$
$NH_2 \cdot OH$	165
Imidazole	128
4-Methylpyridine	1.2
Pyridine	0.32
Nicotinamide	0.03

[a] Data from Khan & Kirby (1970) and from Kirby & Varvoglis (1968)

The best known examples of successful chemical intervention with phosphorus compounds are the organophosphorus poisons, which are phosphorylating agents of the fully esterified type (1) with X = OR′, SR′ or F. These reagents work *in vivo* by phosphorylating the active site hydroxy group of acetylcholinesterase (see Dr Inch's paper), and they also inhibit certain proteolytic enzymes *in vitro* by the same mechanism. They thus act on enzymes catalysing the transfer not of phosphate but of acyl groups. Their activity must therefore be regarded as something of an accident, a consequence of the high reactivity of these reagents towards good oxygen nucleophiles.

An interesting, but much more difficult, proposition is the rational design of reagents to interfere with enzymes catalysing phosphate transfer. Consider the problem for the general case of the transfer of the PO_3^{2-} group from R^1O to R^2O.

$$R^1O \underset{O}{\overset{O^-}{\diagdown}} P \underset{O^-}{\diagup} \quad + \quad R^2OH \quad \rightarrow \quad R^2O \underset{O}{\overset{O^-}{\diagdown}} P \underset{O^-}{\diagup} \quad + \quad R^1OH$$
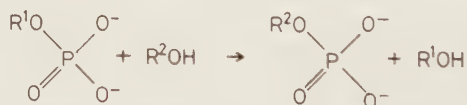
The scope for structural variation here is clearly limited, especially when one considers that many enzymes are specific enough to distinguish phosphate groups from sulphate groups. Perhaps the most effective variation is the replacement of P by As; arsenate is taken up in place of inorganic phosphate in oxidative phosphorylation in some systems, but the arsenate esters formed are much more labile than the corresponding phosphates (see Professor Williams' paper, p. 105), and their premature breakdown leads to the uncoupling of the oxidative phosphorylation process (Corbett 1974).

Alternatively one can substitute one of the negatively charged oxygen atoms, particularly by S or F, and compounds like (13) and (14) have been

made and tested in a few systems, with interesting rather than dramatic results.
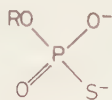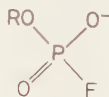
(13)   (14)

The readily available phosphorofluoridates (14) might repay more detailed investigation in the context of the transfer of phosphate.

Finally, one can be sure of inhibiting the phosphate transfer reaction by replacing the oxygen atom at the leaving group by a carbon atom. The geometry about a CH_2 group is slightly different, which means that enzymes may not bind such phosphonate analogues of phosphate substrates, but compounds like the analogues of ATP (15) and (16) have some interesting biological activity (Yount 1975). Much current work in biochemical laboratories is concerned with the use of phosphonate analogues of phosphates in many metabolic reactions and control processes, and we can expect to hear a great deal more about reagents of this sort.
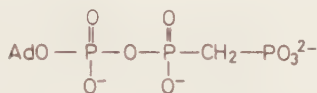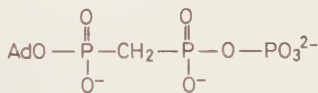
(15)   (16)

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Discussion

Shaw: Is metal catalysis more or less effective in general than proton catalysis?

Kirby: If the metal stability constants are right, the metal can be present in much higher concentration than protons. Therefore, at pH 7, say, metal catalysis is always potentially more efficient than proton catalysis.

Shaw: I have analysed in detail the P–N bond and the effect on bond length (admittedly in the solid state) of methylation or protonation which confers an integral positive charge on the nitrogen atom. This effect is much more dramatic than the effect of coordination by nitrogen to a metal where the charge transfer is apparently less important. How it effects reactivity is another matter.

Kirby: In bonding to metal, a full covalent bond is not formed.

Shaw: The monomeric metaphosphate ion PO_3^- (10) structure is unlikely in biological systems. Is there any spectroscopic evidence for it? Both Niecke's group and Scherer's group (see Shaw 1977) have isolated the analogous nitrogen compounds, e.g. (17), and studied their crystal structures. These species that Westheimer and others speculated about can now be synthesized, isolated and studied, even though their reactivity is high.

$$Me_3Si-N-P(=N-SiMe_3)(=N-SiMe_3) \text{ with } Me_3Si \text{ on N}$$

(17)
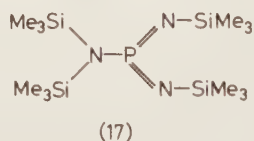
Loughman: Dr Kirby, you said that the inhibitory activity of the substituted phosphate ester (1) on proteolytic enzymes was something of an accident. Do they inhibit the phosphate transfer enzymes such as phosphoglucomutase and the other mutases as well as the acyltransferases or are such inhibitory activities isolated examples?

Kirby: I have concentrated on the well known examples, and there are exceptions. Phosphorylating agents do inhibit a few nucleophilic enzymes of

other sorts, including an acid phosphatase from rabbit and yeast pyrophosphatase (Heath 1961). But known cases involve enzymes catalysing acyl transfer, and there is no general pattern of reactivity towards enzymes catalysing phosphate transfer.

ORGANIC PHOSPHORUS IN THE SOIL

Brydges: Dr Kirby illustrated the reactivity of these organic phosphates but what is the form of the mass of refractory organic phosphates that are in soils? Can they be quickly mobilized chemically?

Loughman: Much of the phosphate is in inositol hexaphosphate.

Tinker: The phosphates are mostly phosphate monoesters, with roughly 25% as inositol hexaphosphate, which is extremely stable in the soil, but about half the phosphorus in organic combination in most soils is probably in unknown compounds.

Harrison: Some of the organic phosphate in soils is polymeric; phosphorus-containing polymeric compounds with molecular weights of 5×10^4 can be found in soils but they have not been characterized (Thomas & Bowman 1966).

R. J. P. Williams: Are they polyphosphates or polysaccharides with attached phosphate groups, such as inositol phosphate?

van Wazer: Polymers with ionic linkages could be built up by complexing of metal ions (e.g. Ca^{2+}) by inositol hexaphosphate molecules to give amorphous masses.

Tinker: There is no evidence to indicate phosphate polymers (in the sense that it is the phosphate group that bonds the polymer); most of the organic matter in soil is an undefined polymeric form and this may have phosphate esterified to it.

Emsley: If the diesters are more stable, why do they not persist longer? Why don't we find a lot of DNA polymer residues in the soil?

Kirby: For a start there are far fewer diesters than monoesters in living organisms.

R. J. P. Williams: Is the inositol phosphate in an insoluble form?

Tinker: It usually exists in soil as the iron or calcium complex, possibly associated with other organic compounds. These complexes are highly insoluble.

Kirby: Are these salts tightly complexed?

Tinker: Yes. Most phosphate monoesters are probably complexed on the soil colloid surfaces almost as tightly as orthophosphate itself.

Emsley: Are all the isomers of inositol hexaphosphate equally inactive or is one prevalent?

Tinker: Different isomers are present. They are degraded slowly otherwise the soil would eventually fill up with it! They owe their stability to the formation of iron complexes or they are strongly adsorbed on some of the many sesquioxide surfaces in the soil—presumably, a geometric factor renders the adsorbed material stable because the appropriate enzyme cannot approach it.

Kirby: Are you saying that soil enzymes are not very effective by themselves in solution in the soil?

Tinker: If their substrate is in solution and has low molecular weight they may work well, but not much phosphate ester substrate exists in that form in natural soils.

Kirby: Microorganisms are unlikely to take these polymers in through their membranes, so any breakdown will be outside the organism.

Pirie: Some microbial phosphorus compounds are extraordinarily stable against acid attack. We worked on one from an organism which does not inhabit soil *(Brucella melitensis)* and had to boil it for days in strong acid to mobilize the phosphorus (Miles & Pirie 1939). Its nature, as far as I know, is still unknown. One would expect a slow accumulation of these very insoluble compounds if they are as resistant to enzyme attack as they are to acid attack.

R. J. P. Williams: But is use of H^+ alone as an attacking group the best approach?

Kirby: The solubility is probably more important than anything else.

Loughman: Plants store phosphate in their seeds in inositol hexaphosphate, and its biosynthesis consumes a lot of ATP. In some higher plants such as flax the plant itself contains surprisingly high concentrations of the hexaphosphate. Some years ago, Morton suggested that it was used directly as a phosphorylating agent (although there is little evidence for this), just as it had been proposed that the yeast polyphosphate granules might be used directly as phosphorylating agents. Recently Biswas *et al.* (1977) have demonstrated direct transfer of phosphate in seeds from inositol hexaphosphate to GDP to give GTP and inositol pentaphosphate and also to ADP to give ATP. Direct phosphorylation of ADP to provide ATP in the early stages of germination, when the mitochondria are hardly active and cannot supply ATP, could be the function of inositol hexaphosphate. If inositol hexaphosphate is much more metabolically active than hitherto supposed, we shall have to revise our ideas about its function. Obviously it is a store of phosphate, because one of the first events in some germinating seeds is its hydrolysis by phytase. In plants one finds only inositol hexaphosphate

and orthophosphate but in soils the complete spectrum from the hexaphosphate to the monophosphate is found mainly as a result of microbial action.

R. J. P. Williams: Like plants, animals store phosphate, but in a totally different way. Not only can they metabolize bone but they also use a protein called phosvitin (certainly this is so for birds and reptiles). This protein is made in the liver and transferred to the egg. There are other phosphoproteins in teeth. Phosvitin contains serine as roughly every third amino acid, and the serine is phosphorylated. So the yolk of an egg contains a huge quantity of serine phosphate. The protein resembles inositol phosphate in the sense that the molecule possesses many phosphate groups, all close together. As one phosphate is removed on hydrolysis the property of the next one (and so the whole protein) changes.

Loughman: The same applies to casein in milk except that it contains less phosphate.

Pirie: Why isn't threonine phosphorylated to the same extent as serine? Rask *et al.* (1970) give ratios of phosphorylated threonine/serine of between 1/8 and 1/33 in five different tissues (see also Taborsky 1974 for phospho-threonine).

R. J. P. Williams: I don't know. The other hydroxy amino acid, tyrosine, won't be phosphorylated because a phenolic phosphate is unstable.

Pirie: Why is no enzyme a phosphoprotein? Enzymes use carboxy and amino groups, why not phosphoryl groups?

Kirby: No enzyme uses a phosphate group catalytically (although enzymes are often phosphorylated as part of the phosphate-transfer process).

R. J. P. Williams: Amino acids already have acid functions so why should they use a phosphoryl group (i.e. less stable group)?

Kirby: Pepsin, for example, extends its pH range by adjusting the pK_a of one of its carboxy groups to be just as acidic as a phosphoric acid.

R. J. P. Williams: Human lysozyme has a pK_a of 7 from a carboxy group. Perhaps enzymes have no need for phosphoryl groups.

Tinker: One of the groups attached to the phosphate in humic acids is a polymer. Would the soil phosphatases see it as an 'R' group even if it has a molecular weight of perhaps 10^5–10^6 or more?

Kirby: The molecular weight does not matter too much. What is important is the structure of the active site of the enzyme because the phosphate may protrude from one side of the molecule; if the site is enclosed then the substrate will not be able to approach, but if it is on the surface the enzymes can work.

Tinker: Swift & Posner (1972), who have separated the different mol-

ecular-weight fractions of organic matter in soil, found that the P/C ratio increases with molecular weight, almost as though a larger molecule stabilizes the ester bond.

Kirby: What is the range of molecular weights? Is inositol hexaphosphate above or below the average?

Tinker: The molecular weights of humic acids increase from about 10 000, i.e. much greater than that of inositol hexaphosphate.

van Wazer: What is the P/C ratio?

Tinker: It is usually very small (around 1/100, w/w).

van Wazer: If the large polymers with a small P/C ratio have a more or less random arrangement and if these compounds of lower molecular weight are degradation fragments of the larger polymers, these fragments should contain less phosphorus than the parent molecule since unesterified phosphates should have a high probability of formation.

Tinker: Does that imply that the surfaces of the big polymer are more likely to have the phosphorus hydrolysed off?

van Wazer: Yes.

Tinker: Nobody knows how these reactions go but it seems more likely that phosphate groups are on average least available in large molecules and this may be why the P/C ratio increases with molecular weight.

van Wazer: One could look at this from an equilibrium viewpoint rather than a kinetic one. Dr Tinker's argument seems to work more qualitatively because of the linear free-energy relation.

Let us consider a system consisting of molecules made up of atoms Q bonded to monofunctional blocking groups G. We can generalize about long-term reactions of these molecules as they meet and exchange groups (by condensation, decondensation etc). All molecules will do this sooner or later; the chemistry of carbon is unique because carbon compounds are particularly slow to undergo exchange of parts. In phosphorus chemistry the rate of exchange of parts is much faster than in carbon chemistry. Let us say that Q is tetravalent; thus a given Q can be surrounded by any combination of Gs and Qs from four Gs to four other Qs. In these long-term reactions (which can be speeded up by heat and catalysts) it appears that, during the rearrangements involving the making and breaking of Q–Q bonds, G groups tend to clump on some Qs and Q atoms cluster on other Q atoms. In other words the Q atoms tend to be found in an environment of either as many Qs or as many Gs as possible. This is the consequence of free-energy considerations, depending on the non-additivity of bond energies. (Bond energies themselves are not involved because the number of bonds is the same if the number of Qs and Gs remains constant.) This mechanism is involved in chemical ageing processes

in general and, I imagine, in the behaviour of humic acids in soils over a long time (in which case one of the class of G groups is the phosphate). When G is hydrogen, some of the rearrangement products will have low molecular weights and will tend to be lost as gases—in long-term ageing of organic substances it is observed that the H/C ratio goes down. When G is phosphate the compounds consist of carbon networks and compounds in which the phosphate groups tend to agglomerate.

Tinker: But if bond energies are not additive and do not influence each other, surely the arrangement will simply be statistically random?

van Wazer: Random statistics are relevant to a certain extent, but it is the non-additivity of bond energies (which may be several kJ/mol) that is the driving force in these reactions. (For a more detailed discussion see van Wazer 1969.)

R. J. P. Williams: In other words, this is true for bond energies $G–Q–G >$ $2G–Q$ for, say, phosphate ($G = PO_4$) on a sugar ($Q = C$).

van Wazer: Or hydrogen on carbon.

R. J. P. Williams: Certainly it is true for hydrogen bound to carbon. For example, sugar, $C_6H_{12}O_6$, in which every carbon has the same environment (HCOH), is less stable than acetate ($CH_3 \cdot COOH$), into which it is converted. Acetate, although it has the same empirical composition $[CH_2O]_n$ has three hydrogen atoms on one carbon atom and two oxygen atoms on the other. Glucose has one hydrogen and one hydroxy group on each carbon atom. The argument says that in the organic matter in soil one set of compounds which has been produced biologically will re-equilibrate into some thermodynamically more stable system which biological systems find particularly hard to handle.

Tinker: That seems to imply that any one humic acid molecule in the soil is likely to accumulate phosphate on it, whereas other polymers will not. Is that true?

R. J. P. Williams: It may not be. Biological systems seem to be better equipped enzymically to cope with material as it dies or decays than with the product of 20–30 years' or more residence in the soil. How is it that during evolution biology has left this phosphate alone? It must be extremely difficult to mobilize, otherwise some organism would have adapted to this massive deposit of carbon, hydrogen and phosphorus and would have had enormous advantages.

Pirie: There are many analogies. Take, for instance, sporopollenin. That persists as a component of fossils for 2000–3000 million years. No organism seems to have found a method for metabolizing it.

R. J. P. Williams: No, but we are considering phosphate transfer in organic

material.   Phosphatases exist, but they transfer phosphate to water.   Why are they so ineffective on this polymeric material?

van Wazer: Because complicated network polymers cannot fit into the active site (the lock-and-key structure) of the enzyme.

R. J. P. Williams: Phosphatases are not very discriminating—they attack most phosphates.

van Wazer: Most *soluble* phosphates.

Tinker: And the rest of the molecule must keep out of the way.

R. J. P. Williams: Or it is digested away.   Presumably microorganisms such as those we have discussed release phosphatases to get at the phosphorus.

Tinker: One cannot be certain of that.   We often assume that root-surface and bacterial phosphatases are excreted to carry out some function.   But how far can they progress through the soil?   Presumably, being proteins, they are adsorbed rapidly on various organic and inorganic surfaces where they would not be able to hydrolyse soluble organic phosphates in soil solution.   Furthermore, I know of no direct evidence that these phosphatases liberate phosphate.   If they did, one should be able to detect an increase in Professor Larsen's 'L' value (see p. 195 [he is too modest to point out that that 'L' stands for Larsen, by the way]).

This seems to be the crux of the matter: all that phosphorus in the polymeric soil organic matter must be inert.   If one could design a soil organic matter, which contained no phosphate, it would presumably function as well in forming the structure of soil and other properties of the organic matter of soil.

Brydges: When I asked about the dense growth in the Cambrian era (p. 90). I was answered that the reason was the same as for jungles today—there was a tremendous recycling of phosphorus.   But all the subsequent discussions deny that; now it seems that as more organic matter builds up more phosphorus is converted into an unavailable form.

Tinker: All soils differ.   In some soils organic matter with its phosphorus builds up.   But the main factor in soils supporting jungles (e.g. Amazon, Congo Basin soils) is the low content of organic matter.   Any organic matter fed into such soils is rapidly metabolized.

Inch: What is the total phosphorus content of those soils?   Usually only richly organic soils are analysed to facilitate the analysis, but most soils are not highly organic soils.   Do phosphates build up in those or are they more easily leached?

Tinker: Soils in forests (similar to rain forests) in Nigeria contain inositol hexaphosphate, but in general little work has been done on such soils.

Loughman: We have talked about many hundreds of thousands of tonnes in so-called organic phosphate besides inositol hexaphosphate but is this

covalently-bound phosphate or inorganic polyphosphate adsorbed within an organic matrix? Several plants make inorganic polyphosphates and sometimes use them as a specific storage form for later use (Jeffrey 1964). Plant roots contain several inorganic pyrophosphatases which can split long-chain inorganic polyphosphates.

Tinker: Also, what happens to fertilizer polyphosphates in the soil?

McClellan: Generally speaking they do not persist longer than a few days or weeks. I imagine that polyphosphates would not be an important component.

Griffith: It depends on conditions; pyrophosphates will persist at and above neutral pH with half-lives of 2000 years. Deposits of calcium pyrophosphate (as pyrophosphate) are known; Shepherd reported these in the late 1800s and he was probably correct.

McClellan: How did he analyse them?

Griffith: By calcium/phosphorus ratio.

McClellan: There is only one known reliable report of pyrophosphate in natural material that is not organic material. Unless the formulation as pyrophosphate can be proved by chromatography I don't put much credence in it. Calcium and phosphate can combine in 50 different crystalline forms.

R. J. P. Williams: Is the surface of soil the catalyst for phosphate transfer?

Inch: It may be. Some experiments on the decomposition of pesticides and sterilization of soils give conflicting results depending on whether sterilization is done by heat treatment or by γ-irradiation, for example.

Some of the anomalous results may be the consequence of changing the surface of the soil during the sterilization—the surface characteristics of the polymers may be altered so that new surfaces are brought into action. Sometimes sterilization increases the breakdown of materials when the purpose was to decrease the breakdown.

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The biological importance of organophosphorus compounds containing a carbon-phosphorus bond

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Abstract Organophosphorus anticholinesterase compounds may be derivatives of phosphoric acid or of a phosphonic acid. The phosphonic acid derivatives are usually more reactive and more toxic than the phosphoric acid derivatives. Examples are given to show that differences in the chemical and biological reactivity of phosphates and phosphonates reflect many different aspects of their chemical structure.

Some recently discovered naturally-occurring phosphonates are described, together with some synthetic phosphonate analogues of naturally-occurring phosphates. The utility of these synthetic phosphonates as tools for probing enzymic reaction sequences is discussed.

Organophosphorus esters, for example (1)–(4), are widely used as insecticides (Eto 1974; Fest & Schmidt 1973). They act as insecticides because they are anticholinesterases, that is they inhibit cholinesterase and prevent the natural hydrolysis of the neurotransmitter acetylcholine. The mechanism of inhibition of cholinesterase by phosphorus compounds is strictly comparable to the mechanism of hydrolysis of acetylcholine (AcCh) by cholinesterase (EH in reactions 1 and 2) with the all important difference that, whereas deacety-
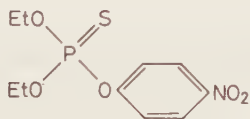
(1) Parathion
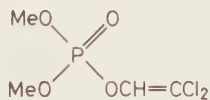
(2) Dichlorvos, Vapona
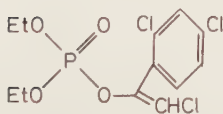
(3) Chlorfenvinphos, Birlane

(4) Diazinon

135

$$EH + AcCh \rightleftharpoons EH \cdot AcCh \rightarrow EAc \xrightarrow{+H_2O} EH + AcOH \tag{1}$$

$$EH + PX \rightleftharpoons EH \cdot PX \xrightarrow{\text{very slow}} EH + POH \atop + H_2O \tag{2}$$
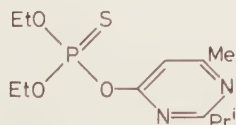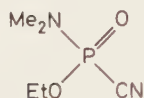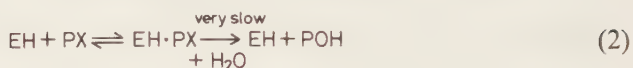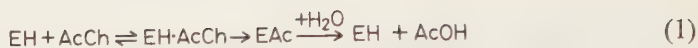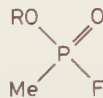
(5) Tabun (GA)   (6) Sarin (GB), R = isopropyl
                   (7) Soman (GD), R = pinacolyl
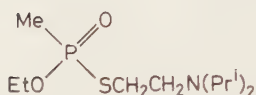
(8) VX

lation is instantaneous, dephosphorylation occurs slowly if at all (Aldridge 1971) (PX is an organophosphorus inhibitor).

Those organophosphorus anticholinesterases that have been selected for use as insecticides are relatively more toxic to insects than to animals and man and can accordingly be used safely in controlled conditions. However, other organophosphorus compounds are so toxic to animals and man that their use as insecticides is precluded. Indeed, many organophosphorus compounds such as (5)–(8) have been considered as potential chemical warfare agents and approach the toxicity of some of the most toxic chemicals that are natural products (Table 1) (SIPRI 1972).

TABLE 1

Relative lethalities of natural poisons and some organophosphorus anticholinesterases relative to Sarin (6) (= 1)

Toxicity	Anticholinesterase	Natural poison
10^{-5}–10^{-6} more toxic		Botulinal toxin A, α-fraction
1000 × more toxic		Batrachotoxin (kokoi arrow poison)
100 × more toxic		Tetrodotoxin, saxitoxin
10 × more toxic	Soman, VX	Ricin, D-tubocurarine, kokoi arrow poison
10 × less toxic	Tabun	Strychnine
100 × less toxic	Parathion	Nicotine

TABLE 2

Toxicity of related phosphates and phosphonates

Compound	LD_{50} (mg/kg)
Pr^iO, Pr^iO — P(=O)(F)	0.45 (i.v., rabbit) 1.4 (s.c., rat)
Pr^iO, Me — P(=O)(F)	0.017 (i.v., rabbit) 0.062 (s.c., rat)
EtO, EtO — P(=O)($SCH_2CH_2N(Pr^i)_2$)	0.07 (s.c., guinea pig) 0.08 (i.v., rabbit)
EtO, Me — P(=O)($SCH_2CH_2N(Pr^i)_2$)	0.009 (s.c., guinea pig) 0.009 (i.v., rabbit)

The compounds too toxic for use as insecticides usually contain a carbon–phosphorus bond and are phosphonates whereas most insecticides do not contain a carbon–phosphorus bond and are phosphates. (There are many exceptions to this generalization). Some comparative toxicity data for closely related phosphates and phosphonates are given in Table 2.

On the basis of such comparisons and since, from a consideration of the relative electron distribution in phosphates and phosphonates, the latter should be more susceptible to nucleophilic attack at phosphorus (Kirby & Warren 1967), many attempts have been made to show that there are correlations between basic hydrolysis rates, anticholinesterase activity, insecticidal activity and mammalian toxicity. The outcome of such studies is the demonstration that correlations exist only within limited series of compounds; correlations are not generally found because in most cases factors such as stereochemical effects, chemical stability, and rates of metabolism are of over-riding importance (Fukuto 1971; Dauterman 1971; Hollingworth 1971). From the many well documented studies that have been reported it is clear that *in vivo* many competing processes are in operation and that small changes

in the relative rates of these processes, which may be caused by changes in the chemical structure of the organophosphorus compound, can have a marked effect on the observed biological properties. Rather than by surveying a large topic, I may illustrate the difficulties that are encountered in attempting to assess the effects on biological activity of small changes in chemical structure by recent results which show that the effect of replacing an oxygen–phosphorus bond by a carbon–phosphorus bond may be much more subtle than the effect of simply increasing the electrophilicity of phosphorus.

EFFECT OF ABSOLUTE STEREOCHEMISTRY

As most organophosphate insecticides are achiral, there is little information about the relation between biological activity and absolute stereochemistry for these compounds. However, the results from studies of the enzymic, insecticidal and mammalian properties of many enantiomeric pairs of chiral phosphonates have clearly demonstrated that anticholinesterase activity is strongly affected by the absolute stereochemistry at phosphorus (Fukuto 1971; Boter *et al.* 1971; Keijer & Wolring 1969). Until recently it was tacitly assumed that the effect of absolute stereochemistry on reaction rates was simply to determine the magnitude of the anticholinesterase activity, insecticidal and mammalian toxicity. Now results have been obtained which indicate that qualitative as well as quantitative differences in biological properties can arise from differences in absolute stereochemistry (Hall *et al.* 1977).

During recent attempts to clarify some aspects of the therapeutic properties of oximes and anti-acetylcholine drugs against poisoning by organo-phosphorus anticholinesterases, it was observed that, whereas a mixture of atropine and pyridine-2-aldoxime methylmethanesulphonate (P2S) provided considerable protection against poisoning by *(S)*(−)-ethyl *S*-propyl methylphosphonothioate, the same mixture provided insignificant protection against the enantiomer *(R)*(+)-ethyl *S*-propyl methylphosphonothioate. Further, more detailed comparisons (Table 3) showed that whereas *in vitro* the

TABLE 3
Comparison of enantiomers of Me(EtO)PO(SPr)

Property	(+)-*Isomer*	(−)-*Isomer*
Anticholinesterase activity	1.01 mol^{-1} s^{-1}	15.01 mol^{-1} s^{-1}
LD$_{50}$ (mice)	2.47 μmol/kg	12.3 μmol/kg
Enzyme-oxime (*in vitro*)	Yes	Yes
Enzyme-oxime (*in vivo*)	No	Yes
Protection by oxime/atropine	No	Yes

stereodependence was simply shown by differences in reaction rates, it was probable that *in vivo* some metabolic modification of the (+)-isomer occurred which caused poisoning not responsive to the conventional therapy. Only in this way is it possible to explain why *in vitro* reactivation of enzymes inhibited by both enantiomers can be effected by oximes whereas *in vivo* only enzymes inhibited by the (−)-isomer and not the (+)-isomer are reactivated by oxime treatment. This difference at the enzyme level is reflected in whole animals by the failure of those poisoned by the (+)-isomers to respond to oxime/atropine treatment.

IMPORTANCE OF PSEUDOROTATIONAL PROCESSES

When a tetracoordinate organophosphorus derivative undergoes nucleophilic attack at phosphorus a pentacoordinate trigonal bipyramidal intermediate can result in which the entering nucleophile and the leaving group immediately occupy apical positions with the leaving group departing from the apical position. Such a reaction occurs with inversion of configuration at phosphorus and is illustrated in Scheme 1. In other circumstances the leaving group need not initially occupy an apical position but reaches that position, from which it departs, only after a permutational isomerization process known as a pseudorotation. The steric outcome, illustrated in Scheme 2, is a nucleophilic displacement at phosphorus with retention of configuration.
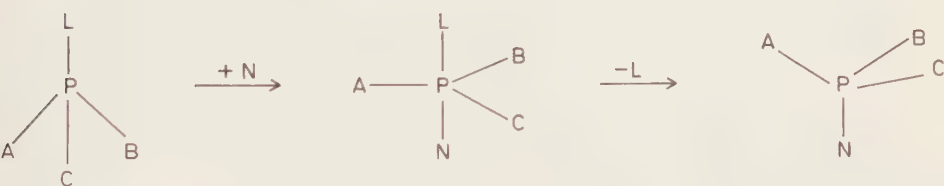
SCHEME 1. Inversion
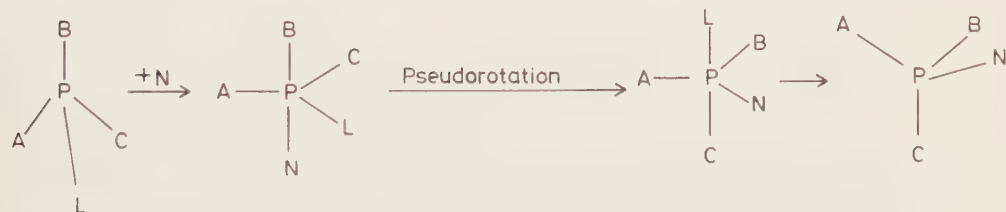
SCHEME 2. Retention

The many factors which determine whether or not pseudorotation is a favoured process, although not completely understood, have been reviewed in considerable detail (Luckenbach 1973). One firm conclusion is that the C–P bond, unlike the C–O–P grouping, provides a considerable restraint on pseudorotational processes. Thus the result that sodium methoxide displaces the thiopropyl group from ethyl S-propyl methylphosphonothioate with inversion of configuration but that similar displacements from alkyl S-alkyl phosphorothioates occur with retention of configuration was not unexpected (Inch *et al.* 1975). Indeed the difference in the steric course of these reactions has been suggested to be the reason why the phosphonothioates in Table 4 are hydrolysed by hydroxide more slowly than the corresponding phosphorothioates. These hydrolyses are not consistent with the usual pattern observed for phosphono and phosphoro derivatives which supports the theory that phosphoro compounds are hydrolysed less readily and are less susceptible to nucleophilic attack at phosphorus than their phosphono analogues because electron release from substituents with lone pairs of electrons increases the electron density at phosphorus making bond formation with the nucleophile more difficult.

Although the alkaline hydrolysis rates for the thioates were anomalous, the biological results were not; the rates of cholinesterase inhibition (Table 4)

TABLE 4

Rates of hydrolysis by hydroxide and inhibition of acetylcholinesterase of phosphonothioates and phosphorothioates

Compound[a]	Second-order hydrolysis rate,[b] $k_{OH}/l\ mol^{-1}\ s^{-1}$	Second-order rate constant of inhibition of acetylcholinesterase ($l\ mol^{-1}\ s^{-1}$)
Phosphonothioate (A)	3.8×10^{-3}	8.0
Phosphorothioate (B)	6.6×10^{-3}	0.48
Phosphonothioate (C)	0.16	3.2×10^5
Phosphorothioate (D)	0.42	1.3×10^4

EtO   O
    \ //
     P
    / \
  Me   SR
(A) R = Pr
(C) R = CH$_2$CH$_2$N$^+$Me$_3$I$^-$

EtO   O
    \ //
     P
    / \
  EtO   SR
(B) R = Pr
(D) R = CH$_2$CH$_2$N$^+$Me$_3$I$^-$

[a] For comparison k_{OH} values for ethyl methylphosphonofluoridate and diethyl phosphorofluoridate were 52 and 2.9 l mol^{-1} s^{-1}, respectively.
[b] Rates were measured conductiometrically in water containing propan-2-ol (5% v/v), total ionic strength 0.1 mol/l with sodium nitrate.

showed the racemic phosphono derivative to be a better enzyme inhibitor than the phosphoro derivative. This result further emphasizes the difficulties that are encountered when attempting to relate chemical and biological reactivity.

The fact that phosphoro derivatives can undergo pseudorotational processes whereas phosphono derivatives cannot may have other biological implications if situations on the enzyme or other biological material are envisaged where migration of a phosphorus ester from one hydroxy group to another occurs. In model experiments with glucopyranose derivatives (Cooper *et al.* 1974; J. M. Harrison & T. D. Inch, unpublished results, 1977) it has been shown that, in methanol containing sodium methoxide, a diethyl phosphoro group will migrate from O-4 to O-6 without exchange of the ethyl groups with methanol. Clearly the migration involves a trigonal bipyramidal intermediate as illustrated in Scheme 3. In contrast, migration of an ethyl methylphosphono group from O-4 to O-6 occurs with substantial exchange of the ethyl group with methanol. Most probably migration occurs via a cyclic phosphate intermediate as shown in Scheme 4. Although this difference may be little more than a chemical curiosity, the fact that the mechanism of migration favours ester exchange or hydrolysis (i.e. dealkylation) for phosphonate groups may be relevant in some biological situations.
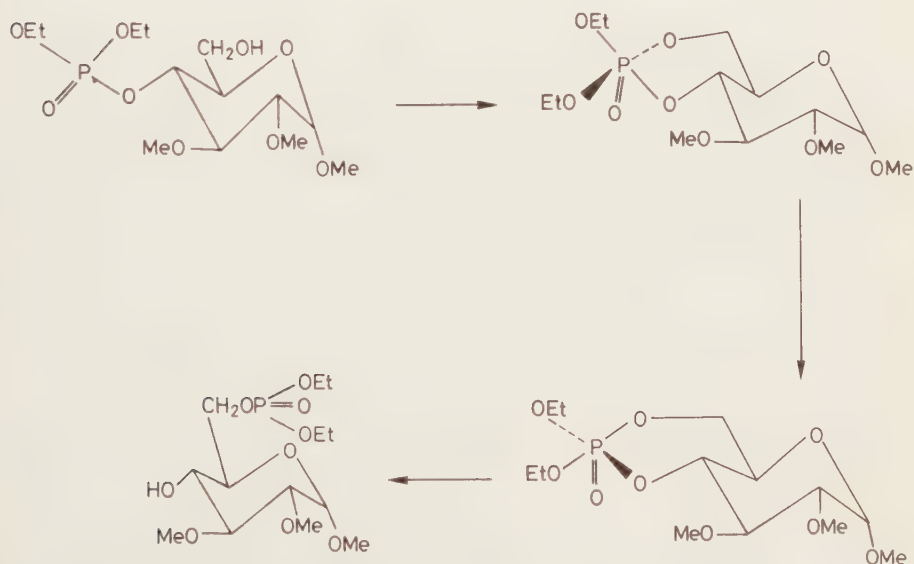
SCHEME 3
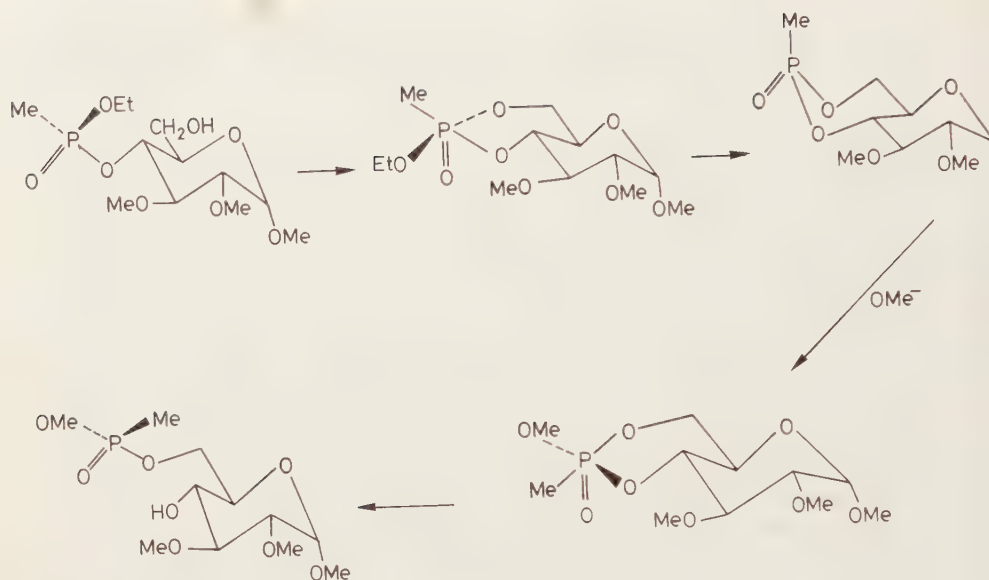
Scheme 4

NUCLEOPHILIC ATTACK AT THE ALKOXY CARBON ATOM

The observed *in vivo* effects of any chemical are a summation of toxic and detoxification processes. For organophosphorus derivatives detoxification can occur by hydrolytic attack at phosphorus or by nucleophilic or oxidative attack at the alkoxy carbon atom. It is important to note, therefore, that, just as phosphonates are more susceptible to nucleophilic attack at phosphorus

TABLE 5

Second-order kinetic constants, for hydrolysis and dealkylation of some organophosphorus compounds

Compound (X = O or S)		X = O	X = S
EtO, Me — P(=X)(O—C6H4—NO2)	$K/[OH^-] =$	3000	400
	$K[thio^-] =$	0.87	0.24
EtO, EtO — P(=X)(O—C6H4—NO2)	$K/[OH^-] =$	44.1	3.6
	$K[thio^-] =$	0.05	0.05

than are phosphates, so are phosphonates more susceptible to attack at the alkoxy carbon atom (Adamson & Inch 1973). The results in Table 5, in which second-order kinetic constants for hydrolysis are a measure of nucleophilic attack at phosphorus and second-order constants for dealkylation by thiosulphate are a measure of nucleophilic attack at carbon, provide an example of this phenomenon. Clearly, in certain situations these effects could counteract each other and provide an outcome in which a phosphonate is equivalent in toxicity to a phosphate.

PHOSPHONATES AS ANALOGUES OF NATURAL PHOSPHATES (recently reviewed by Engel 1977)

Since 1959 there has been a steady discovery of phosphonic acid derivatives (Kittredge & Roberts 1969), most of which are close structural analogues of amino acids (Table 6). Most occur in lipids, although some occur free in the cell, and at least one has been shown to be a component of a specific non-lipid macromolecule, a phosphonoglycan. Another naturally-occurring phosphonic acid is the broad spectrum antibiotic phosphonomycin (9) (Kahan *et*

(9)
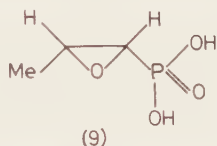
*al.*1974) which has been isolated from *Streptomyces fradiae*. This antibiotic can be administered orally, attacks the cell walls of bacteria and shows little toxicity to the host. Obviously, the identification of these and similar natural phosphonates has stimulated considerable speculation about the nature of biological C–P bond-forming and -breaking reactions but although plausible schemes have been postulated much more definitive work is required.

TABLE 6

Some naturally-occurring phosphonic acids $R^1PO(OH)_2$ and their amino acid analogues $R^2CH_2 \cdot COOH$

R^1	R^2	Reference
$NH_2 \cdot CH_2 \cdot CH_2 \cdot$ (2-amino-ethylphosphonic acid)	$NH_2 \cdot CH_2 \cdot$ (β-alanine)	Horiguchi & Kandatsu (1959), Kittredge *et al.* (1962)
$MeNH \cdot CH_2CH_2 \cdot$ (2-methyl-aminoethylphosphonic acid)	$MeNH \cdot CH_2 \cdot$ (*N*-methyl-β-alanine)	Kittredge *et al.* (1967)
$NH_2 \cdot CH_2 \cdot CH(COOH) \cdot$ (3-amino-2-phosphonopropionic acid)	$NH_2 \cdot CH(COOH) \cdot$ (aspartic acid)	Kittredge & Hughes (1964)

The discovery of natural phosphonates has also stimulated interest in synthetic phosphonates as analogues of various forms of carboxylic acids and as analogues of naturally-occurring phosphates. The hope clearly is that the latter analogues will act by perturbing in some way the regular metabolic processes simply by non-participation in normal phosphate transfer processes. At present the interest is largely in using phosphonates as a tool for elucidating reaction mechanisms rather than in expecting a commercial usage.

The most convenient of the available methods for making phosphonate analogues of natural phosphates are illustrated in Schemes 5-8. For example, the Arbusov or Michaelis-Baker reactions (Scheme 5) have been used to form products which, by comparison with the natural product, lack the oxygen link between phosphorus and carbohydrate carbon (Griffin & Burger 1956). The Abramov reaction (Paulsen *et al.* 1971) gives similar products but with the addition of a hydroxy group on the α-carbon atom (Scheme 6). Various forms of Wittig reaction (Jones *et al.* 1970; Adams *et al.* 1974) (Schemes 7 and 8) lead to the formation of isosteric analogues of natural phosphates in which the oxygen link is replaced by a $-CH_2-$ group. These types of reaction lead to products which may be converted into nucleotide and cyclic nucleotide analogues (e.g. 10–12) (Jones *et al.* 1970).

Griffin & Burger (1956).
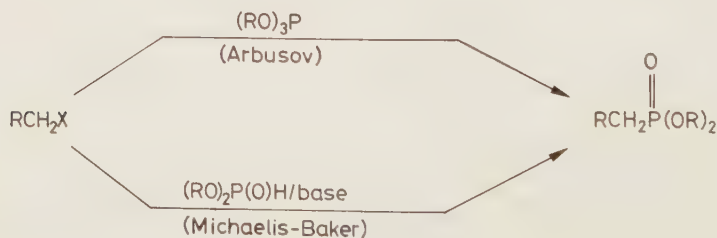
SCHEME 5
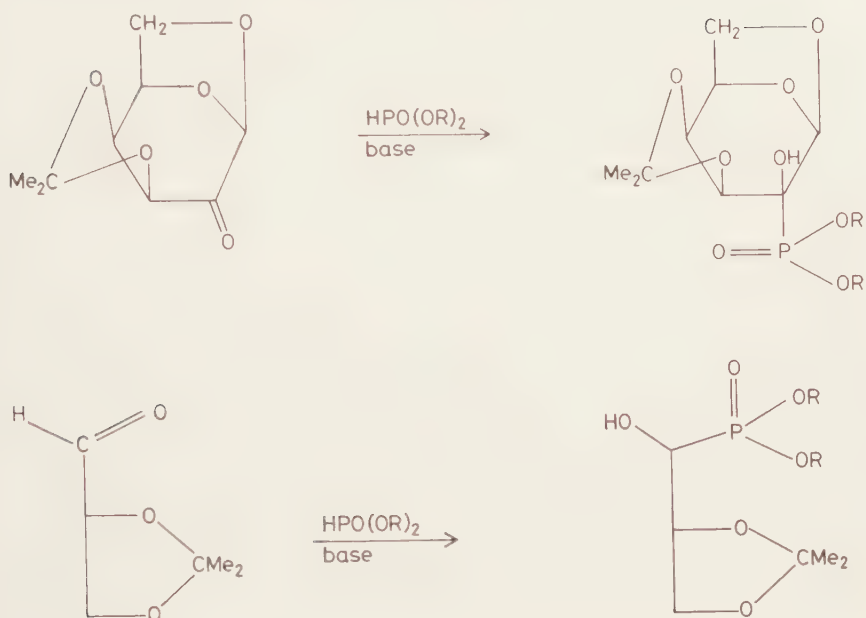
SCHEME 6. Abramov reaction (Evelyn *et al.* 1969; Paulsen *et al.* 1971; Paulsen & Kuhne 1974).
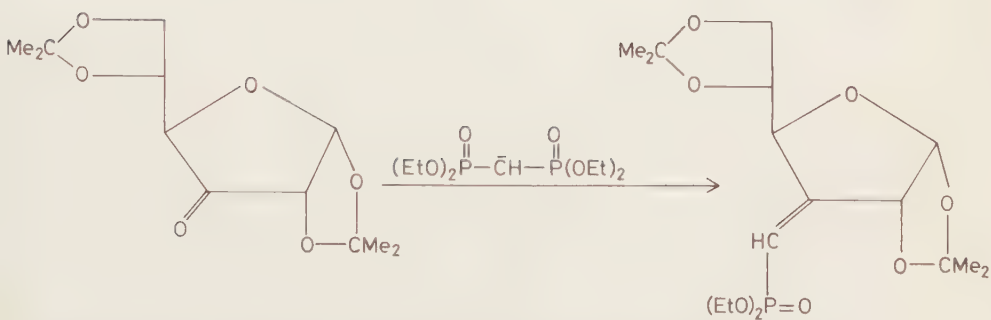
SCHEME 7 (Jones *et al.* 1970), using $(EtO)_2PO \cdot \bar{C}H \cdot PO(OEt)_2$ (Wadsworth & Emmons 1961).

SCHEME 8 (Adams *et al.* 1974).

CH₂OH
|
HO—C—H
|
CH₂CH₂PO₃H₂
(13)

CH₂OH
|
HO—C—H
|
CH₂PO₃H₂
(14)

CH₂OH
|
HO—C—H
|
CH(OH)PO₃H₂
(15)

CH₂OH
|
CHOH
|
CH₂OP(Me)(=O)(OH)
(16)
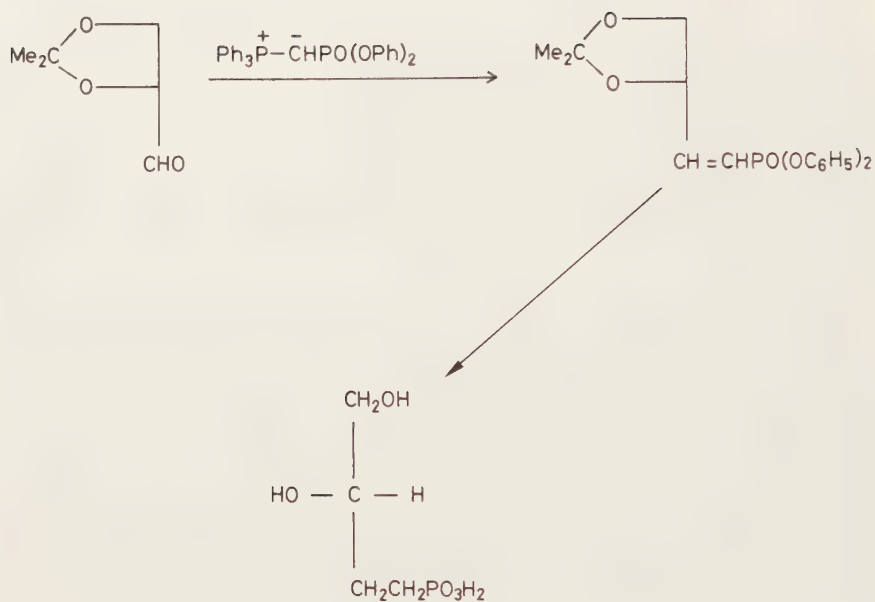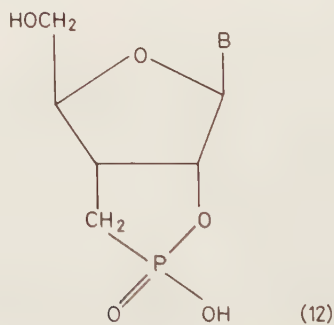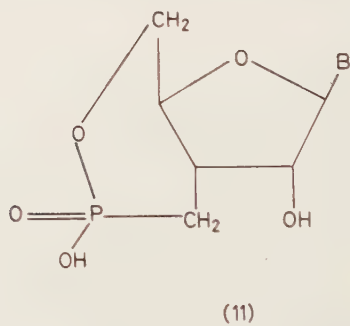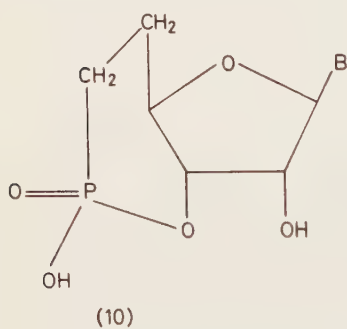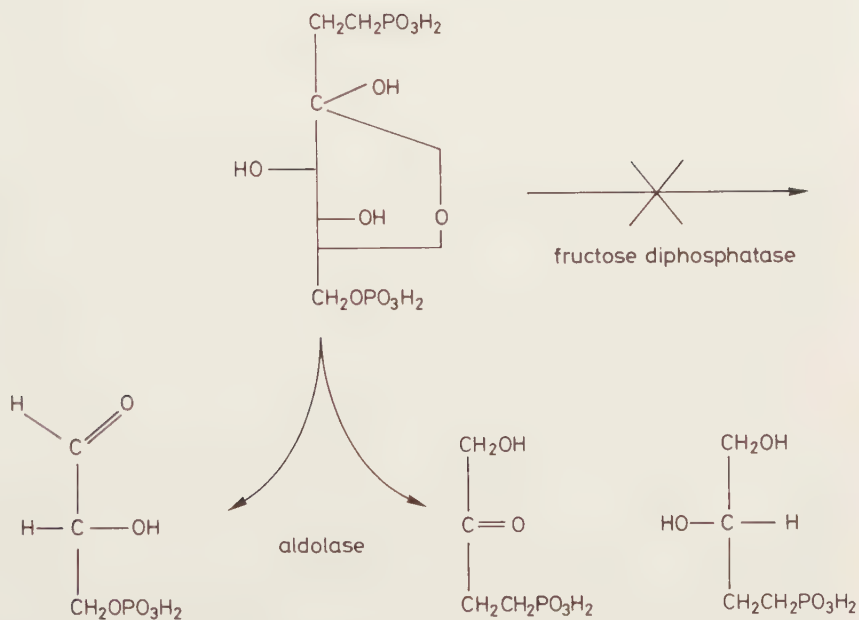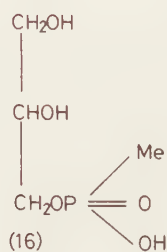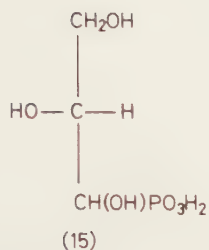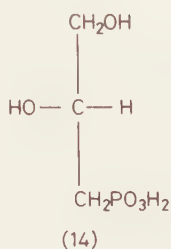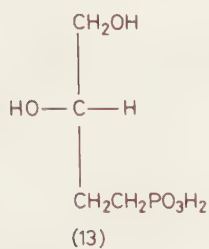
Scheme 9

To date, only compounds containing the $-CH_2-$ link show much promise as true analogues of natural phosphates. For example, the four phosphonate analogues (13–16) of glycerol-3-phosphate have been tested as substrates or inhibitors of glycerol-3-phosphate dehydrogenase from rabbit muscle. Only the derivative containing $-CH_2-$, which was prepared stereospecifically, starting from D-mannitol (Adams *et al.* 1974), was a substrate for the oxidation. The other compounds were neither substrates nor inhibitors.

Perhaps one of the most interesting results is that summarized in Scheme 9 which shows that, whereas phosphonates may be good substrates for reactions which do not involve phosphate transfer, they certainly act as inhibitors of phosphate transfer reactions (Stribling 1974).

I shall not discuss in detail the many studies in which phosphonate analogues of natural phosphates, particularly nucleoside phosphates, have been used. One example is their use as potential anti-cancer agents (Wigler & Lozzio 1972); another is the use of cyclic phosphonate analogues of cyclic phosphates to investigate the stereochemistry of ribonuclease action (Usher *et al.* 1970). In addition to medical utility of phosphonomycin, some analogues of phosphonoacetic acid have been examined for anti-herpes activity (Herrin *et al.* 1977) and some phosphinic acid derivatives have been examined as potential non-steroidal anti-inflammatory agents (Anderson *et al.* 1974). *N*-Phosphonomethylglycine is a promising herbicide that exerts its effect by inhibiting the biosynthesis of aromatic amino acids (Roisch & Lingens 1974).

Further, phosphorus-containing analogues of methadone have been considered as analgesics (Shelver *et al.* 1974) and phosphorus-containing analogues of 1-alkyl-4-phenylpiperazines have some anti-hypertensive activity (Glamkowski *et al.* 1974). Other organophosphorus derivatives have shown hyperglycaemic activity (Blank *et al.* 1975) and some trialkyl-phosphine-gold complexes have anti-arthritic properties (Sutton *et al.* 1972).

The foregoing brief summary provides an indication that there appears to be considerable potential utility in phosphonate analogues of phosphates and other natural products but that much more work is needed to determine whether phosphonates can be exploited commercially.

It must not be overlooked that although this presentation has been concerned principally with compounds containing carbon–phosphorus bonds many organic esters of phosphoric acid itself have wide-scale commercial applications. For example, phosphoric acid esters are used as oil additives—as wear inhibitors, antioxidants, gel agents and for oils that are subjected to extreme pressures. In polymer chemistry phosphorus derivatives find use as light stabilizers, antioxidants, anti-static agents, cross-linking agents and as dispersing agents. In the cosmetic industry phosphorus derivatives are in-

cluded in shampoos as emulsifiers and in toothpaste to prevent tooth calculus. Phosphorus derivatives are also used as fire retardents, anti-flocculants and flotation agents.

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Discussion

Labarre: Dr Inch, you have shown clearly how substitution of a P–C bond for a P–O bond tremendously increases the toxicity of the substance with

respect to rats, rabbits or man. What is not so well known is what happens on substitution of another P–C bond for a second P O bond, thus giving a phosphine derivative. When one substitutes a P–N bond for a P–O bond one obtains the same result: the toxicity increases. But the potential pharmacological activity of the substance also increases greatly. And, often to the surprise of people who are not familiar with the field, treatment of a proliferating disease relies on *toxic* substances. The dream of those people working on anti-tumour compounds was to find a non-toxic, active substance but no example in the drug literature realizes this dream. One has to find the balance: the exact quantity of drug that must be injected to destroy the 'diseased' DNA yet leave the living, healthy DNA. I mention this because if one replaces the P–O bond of a toxic phosphate (with an LD_{50} of a few mg/kg) with a P–C or P–N bond, one might produce a highly toxic but useful drug.

Pirie: Dr Inch, are there enzymes that split the C–P bond?

Inch: There probably are such systems in anaerobic but not in aerobic systems.

Pirie: They don't occur in man, for instance?

Inch: We have no evidence that they do. Anaerobic systems operate in soil and vegetation.

Pirie: Have natural compounds with a C–P bond been found in mammals?

Inch: Yes; for example, 2-aminoethylphosphonic acid has been found in sheep and in sea anemones (see e.g. Karlsson *et al.* 1974).

Shaw: It also occurs in human heart muscle (Cassaigne *et al.* 1978).

Inch: But the number of C–P compounds is negligible compared with O–P compounds.

R. J. P. Williams: You and Dr Kirby described these C–P compounds in animals mostly. What about the compounds and herbicides in plant systems? Do they have any special role?

Inch: No. Methylphosphonic acid, $CH_3PO(OH)_2$, probably stimulates plant growth to a certain extent. Many enzyme systems in plants break down alkyl esters of methylphosphonic acid in the way one would expect dialkyl phosphates to be broken down to phosphoric acid.

Loughman: Ethylene is normally presented as a phosphonic acid derivative (e.g. Ethrel, 2-chloroethylphosphonic acid) when it is used commercially (e.g. in fruit ripening).

Shaw: Are there any metabolic studies on phosphonomycin?

Inch: Not that I am aware of.

J. H. Williams: Insecticidal organophosphorus compounds are degraded rapidly in soil compared with the organochlorine insecticides but soils differ widely. At the extremes there are sandy mineral soils and peaty soils.

Compounds like chlorfenvinphos (see p. 135) and other organophosphorus insecticides have a much longer half-life in peaty soils. We put this longevity down to the fact that the insecticides are highly adsorbed in these soils and are not so available for hydrolysis by enzymes or to attack by microorganisms. What happens in highly organic soils to prevent such compounds being degraded?

Inch: Again it is the availability to the enzyme: organophosphorus insecticides are only sparingly soluble in water and consequently they are adsorbed onto organic material and on other soil material. That limits their mobility (and reduces enzyme activity) and uptake is limited as a result. Many laboratory experiments are done in hydroponic culture solutions which give no indication about uptake from soil especially with regard to these strongly adsorbed materials.

Shaw: We tend to consider that, when something is in solution, it is readily reactive. But this is by no means always the case; for example, the secondary and tertiary structure of polymers can prevent reaction. Although thermodynamically a reaction ought to proceed, if the reagent cannot approach the reactive site solubility *per se* is not enough to guarantee reactivity.

Loughman: Do the cyclic phosphonate analogues inhibit the phosphodiesterase that breaks down cyclic AMP, thereby raising the concentration of the latter?

Inch: It is difficult to interpret the results because, as always with these systems, differences of transport and so on exist *in vivo* and *in vitro*. Anticholinesterase inhibitors, for instance, dramatically alter the concentrations of cyclic AMP and cyclic GMP in the brain; this is part of their toxic action—it is not simply direct action against cholinesterase but a general upset of transmitter processes.

Brydges: If natural compounds exist in humans with C–P bonds that are toxic (even though, as Dr Labarre pointed out, this property may have beneficial or pharmacological effects) what do they do? Are they possibly part of a built-in internal repair mechanism?

Inch: The C–P bond itself is not toxic; the toxicity depends on the other substituents on the phosphorus atom (as Dr Kirby described in his paper). However, the natural purpose of the compounds containing a C–P bond is not clear.

Emsley: Is this difference in reactivity between optical isomers of nerve gases a general phenomenon?

Inch: The isomers of nerve gases show considerable differences in reactivity to cholinesterases. But the example I quoted is the first to my knowledge of any reaction of cholinesterases, whether with nerve agents or

with insecticides, which shows this kind of enantiomeric difference with the (−)-isomer responding to conventional therapy whereas the (+)-isomer does not. Presumably some metabolic activation of the (+)-isomer occurs.

Labarre: Many geometrical isomers show different reactivities. For example, *trans* derivatives of cyclopropane are used as neuroleptics whereas the corresponding *cis* compounds have no activity (see, e.g., Crasnier *et al.* 1975).

Emsley: But in this case, where we know that many nerve gases can be resolved into isomers, it is good to know that the antidotes work for both forms!

Brydges: As thermodynamics seem to control the reactions of these compounds I should have thought that insects and so on should not be able to build up resistance to them. How do they do so?

Inch: They improve the detoxification mechanisms. Humans do this, too. However, other mechanisms also exist. For example, when a person is poisoned with a cholinesterase agent and the body is totally depleted of cholinesterase, particularly in the central nervous system, he can survive a subsequent poisoning with cholinesterase if he can be maintained and supported by artificial respiration and other means for long enough to overcome the first insult. Normal mechanisms seem to be by-passed and alternatives come into action. At least animals do this and we presume that humans do the same.

Tinker: There is a distinction between increased resistance in the individual and the development of resistant strains within the population.

Inch: Yes, but resistance in insects stems from an improvement in their metabolic processes. Insecticides show a wide range of selectivity of effectiveness against different types of insects.

Shaw: In Southern Turkey (and elsewhere) mosquitoes have become resistant to insecticides and consequently the incidence of malaria has increased by orders of 10 over the past 2–3 years.

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Metabolic factors and the utilization of phosphorus by plants

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Abstract The overall process of entry and transport of phosphate by plants has been separated into its component parts. Rapid esterification is involved but a small proportion of the total transport may occur by a non-metabolic route. Mannose alters the metabolism of phosphate in roots of cereals and thereby reduces the transport to the shoot by as much as 99% whereas dicotyledonous species are much less sensitive. The sequestration of phosphate as mannose 6-phosphate is reversible in some species depending on the extent of its conversion into fructose 6-phosphate and it is possible that *in vivo* controls of this type operate in whole plants.

The factors involved in the control of distribution of inorganic phosphate between cellular organelles and throughout the plant are discussed. Enzymic hydrolysis of organic forms by roots and associated microorganisms may also be important in soils where available orthophosphate is limiting. Other inorganic nutrients, particularly boron, play an important role during the transport of phosphate across membranes.

Major differences have been found in the capacities of different species to transport absorbed phosphate to the shoot. Peas and field beans absorb efficiently in the early weeks of growth but the rate of transport is about one thirtieth that of oats, barley, mung bean or sunflower. The relevance of the experimental findings to the wider problem of efficiency of fertilizer use and the possible selection of genotypes with high capacities for absorption and transport are discussed.

The concentration of inorganic orthophosphate in the soil solution is usually in the range 0.1–10 μmol/l even though adequate reserves may be present in other exchangeable labile pools. The only natural form of replenishment of available phosphate is by solubilization of rock components or by the decay of organic matter. Even where the available phosphate is supplemented with added fertilizer the relatively low mobility of phosphate ions may severely limit the transfer to the areas of active absorption by roots. The high rate of

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fertilizer application in the UK in recent years has resulted in the build up of reserves of phosphate in soil because in some cases the amount removed by the crop is considerably less than the amount applied. Some crops show little response to added phosphate whereas others (e.g. potato) need the application of phosphate fertilizer for maximal yield. Increased costs of such fertilizers may well alter this situation and efforts to increase the efficiency of use of such fertilizers are necessary. A knowledge of the mechanisms by which phosphate is accumulated by plants and of the environmental factors that influence the overall process is essential when one considers problems of efficient use of phosphorus, whatever the form in which it is applied. Fundamental research on this problem must necessarily combine biochemical and physiological approaches and in this paper I shall give particular attention to the following aspects:

(1) the mechanisms involved in the process of entry of phosphate into roots;
(2) the mechanisms involved in transport of phosphate through the root and up to the shoot;
(3) factors affecting the selection between absorption and transport;
(4) the fate of absorbed phosphate within the cell;
(5) redistribution within the plant;
(6) the effects of microorganisms on the use of different forms of phosphate;
(7) interactions with other essential nutrients;
(8) differences in use between and within species.

THE MECHANISM OF ENTRY INTO ROOTS

The experimental work described here has been done mainly with young seedlings of barley, grown in controlled conditions, in water culture, as described elsewhere (Loughman 1966). Phosphate is absorbed mainly as the $H_2PO_4^-$ ion and for maximal efficiency of absorption experiments were done at pH 5.5 at 20 °C at a light intensity of 12 700 lx. Apart from the major effects of pH, oxygen tension is also important and the culture solutions were normally aerated to maintain oxygen supply and to provide efficient stirring of the solution in contact with the roots.

The importance of metabolism in the process of entry is shown by the fact that, within five seconds of exposure of the root to $10\mu M$-$KH_2^{32}PO_4$, up to a third of the absorbed ion is incorporated into nucleoside tri- and di-phosphates, nucleoside diphosphosugars, hexose phosphates and other components of the glycolytic system. The rapidity of esterification makes analysis of the overall process difficult; even at 0 °C significant esterification of the small amount of absorbed phosphate occurs. Some less active tissues,

e.g. potato slices, have been loaded with non-exchangeable orthophosphate at 0 °C; subsequent transfer to 25 °C brings about immediate esterification (Loughman 1960). The metabolic process can be uncoupled by 2,4-dinitrophenol; although no esterification occurs the fact that a little phosphate enters the root and shoot suggests that a small proportion of the total absorption may be the result of a passive process (the non-metabolic component of Fig. 1). The bulk of the phosphate in the plant enters by the metabolic route and the pattern of phosphorylation can be followed by iso-lation of the labelled intermediates after short-term exposures. It is perhaps important to point out here that, contrary to the earlier view that only the apical zones of young roots absorb ions, more recent work has shown that older areas of undamaged roots are effective in the absorption and transport of phosphate (Clarkson et al. 1968).

THE MECHANISM OF UPWARD TRANSPORT

Within about 10 min after exposure of the roots of young barley plants to $KH_2^{32}PO_4$ radioactivity can be detected in the stem and, although at this time over 75% of the ^{32}P in the root is in organic forms, almost all that present in the xylem is inorganic (Loughman & Russell 1957). This experiment indicates that a dephosphorylative step is involved in the transfer of phosphate to the upward transport system and support for this view is provided by the obser-vation that inhibitors of phosphatases, e.g. fluoride, have a greater effect on upward transport than on entry into the root. The clear separation of these two processes is an important implication of such experiments and a wide range of treatments can be used to distinguish between them. It appears that separate metabolic mechanisms are needed for entry into the root and entry into the xylem. One of the consequences is that the xylem concentration may reach 1000 times that of the external solution and the mechanism of transfer is clearly highly efficient.

FACTORS AFFECTING THE SELECTION BETWEEN ABSORPTION AND TRANSPORT

The fact that the growth of plants can be maintained in flowing culture solutions at a constant concentration of $1\mu M$-KH_2PO_4 implies that a high-affinity system operates at the root surface. At 0.1 μmol/l entry into the root occurs but transport to the shoot is strongly inhibited because of preferential absorption by microorganisms. The lowered oxygen levels characteristic of waterlogged soils inhibit upward transport more than absorption (Loughman 1966) indicating that the transport process may be more dependent on

oxidative metabolism than is the process of entry or that the oxygen deficit is greater in the stele. Lowered temperature also affects transport rather more than entry and clearly a wide range of environmental changes can significantly affect the relative efficiencies of absorption and transport thereby adding support to the view that separate processes are involved. In addition, environmental changes brought about by agricultural practice (e.g. spraying with herbicides) can also affect the distribution of phosphate within the plant. Neither 2,4-dichlorophenoxyacetic acid nor aminotriazole have much effect on the entry of phosphate into barley roots but, whereas the former reduces upward transport, the latter increases the proportion of absorbed phosphate moving to the shoot by as much as six-fold (Wort & Loughman 1961).
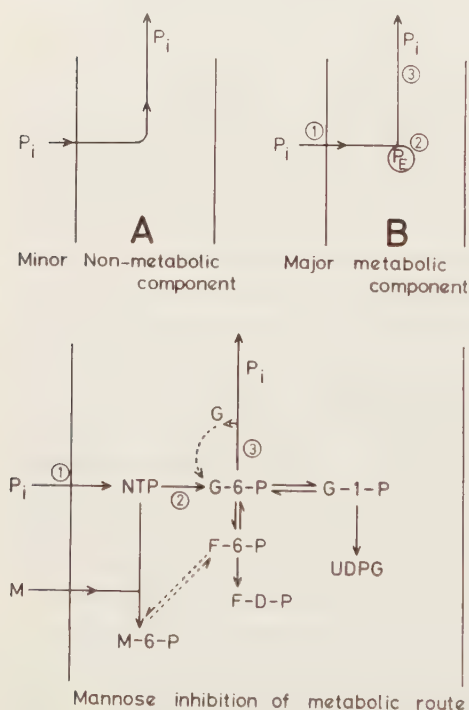
FIG. 1. Possible mechanisms involved in absorption and transport of phosphate in young barley plants: NTP and NDP, nucleoside triphosphates and diphosphates; G, glucose; G-1-P, glucose 1-phosphate; G-6-P, glucose 6-phosphate; F-6-P, fructose 6-phosphate; FDP, fructose 1,6-diphosphate; M, mannose; M-6-P, mannose 6-phosphate; UDPG, uridine diphosphoglucose.

The most striking example of selection between the processes of absorption and transport in cereals is provided by the addition of 100μM-mannose to the root environment. The metabolic pattern in the root is completely altered as a result of sequestration of absorbed phosphate as mannose 6-phosphate and upward transport is inhibited by 95%. As pre-treatment with mannose has no effect, the mannose must cross the membrane with the phosphate for this inhibition to occur. Sensitive cereal species have low activities of phosphomannoisomerase which converts mannose 6-phosphate into fructose 6-phosphate whereas those species in which high activities of the enzyme can be demonstrated, e.g. mung bean, are relatively unaffected by mannose. A normal plant metabolite such as mannose can therefore modify the mechanisms by which the phosphate ion is distributed throughout the plant when supplied at the correct site. The relative activities of enzymes of the glycolytic cycle can clearly modify the control of transport process in ex-perimental conditions and similar control mechanisms may operate *in vivo*. The scheme outlined in Fig. 1 illustrates the possible mechanisms implied by the results of experiments of this type. A notable feature of the mannose
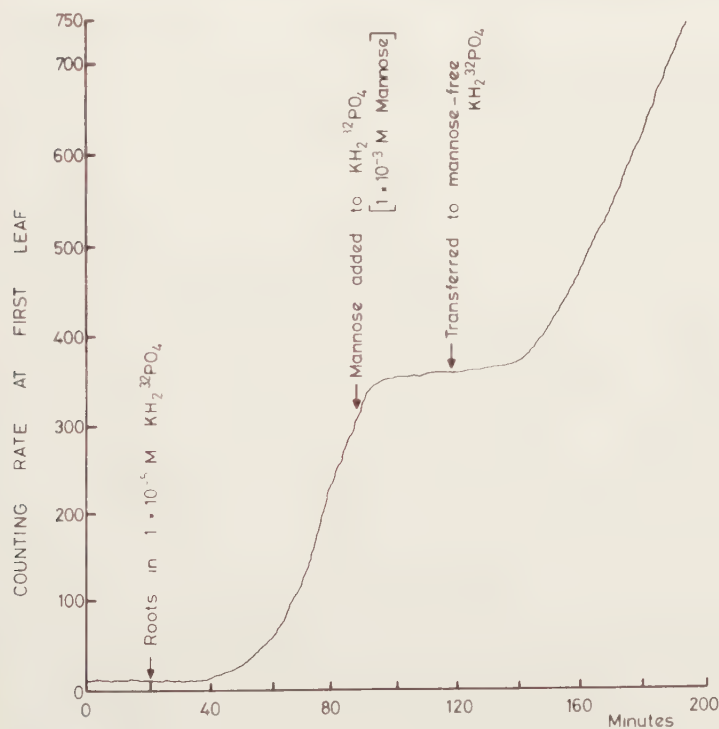
FIG. 2. The inhibitory effect of mannose on the transport of phosphate to the shoot of a young barley plant and the recovery after removal of mannose from the root environment.

effect is the rapidity of onset, shown in Fig. 2. Within a few minutes of addition of 1mM-mannose to the root environment of a young barley plant the transport rate drops almost to zero but is restored within about 45 min after removal of mannose. During this period of recovery the metabolic pattern in the root characteristic of mannose treatment (i.e. 70% of the absorbed phosphate in the form of mannose 6-phosphate) reverts to the control pattern. In the experiment outlined in Fig. 3 the degree of reversal of metabolism was measured after 90 min in the mannose-sensitive species, maize, barley and oats and in the less-sensitive sunflower; mung beans and peas are much less affected by mannose.

The sensitivity to mannose is reflected in the ease with which transport recovers on removal of mannose. Fig. 2 shows that transport recovers within an hour in barley and the chromatogram taken 90 min after removal of mannose shows that the metabolic pattern has returned to normal (Fig. 3). In

FIG. 3. Chromatogram scans of extracts of roots of 12-day-old seedlings of six species: (a) 90 min in 10μM-$KH_2{}^{32}PO_4$; (b) 90 min in 10mM-$KH_2{}^{32}PO_4$ + 1mM-mannose; (c) 90 min in 10μM-$KH_2{}^{32}PO_4$ + 1mM-mannose followed by 90 min in 10μM-$KH_2{}^{32}PO_4$. The chromatograms were developed in t-butanol/water/picric acid (80 ml/20 ml/2.0 g) for 18 h. The scans from maize roots are similar to oats and those from pea are similar to mung bean. The sunflower scans are similar to barley except that the inhibition of incorporation into the nucleoside phosphate peak is not as severe. (See Fig. 1 for abbreviations; PGA is phosphoglyceric acid.)

similar conditions the metabolic patterns of the less-sensitive sunflower return to normal whereas those of highly-sensitive maize and oats remain unaltered. If high sensitivity is correlated with the activity of phosphomannoisomerase, then the rate of reversal is a useful measure of the *in vivo* activity of this enzyme. The low activity of the enzyme in extracts of roots of barley and the high activity in mung beans confirm this trend although one must be cautious in attributing significance to the *in vitro* measurements since the demonstration of a particular enzyme activity is no indication of the functional importance of the enzyme in the normal metabolism of the tissue.

THE FATE OF ABSORBED PHOSPHATE WITHIN THE CELL

The extremely rapid incorporation of inorganic orthophosphate into organic forms indicates that the cytoplasmic pool contains little inorganic phosphate; various calculations based on kinetic experiments estimate that this value may be as low as 1% of the total inorganic phosphate in the cell (Loughman 1960). The transfer of surplus phosphate into the vacuole is also implied by the demonstration that steady-state levels of ATP and other nucleotides change relatively little over a wide range of concentration of applied phosphate; a 30-fold increase in the total level of P in the cell is accompanied by a small change in the cytoplasmic level and the excess appears in the vacuole. In some cases phosphate may be precipitated as insoluble salts in the vacuole but special storage forms may be present. Polyphosphates and inositol phosphates can be found in the cytoplasm and vacuole or even in special storage sites produced for the purpose as in the polyphosphate nodules of *Banksia ornata* (Jeffrey 1964). Particular interest in this aspect of the storage of phosphate arises from the work of Biswas *et al.* (1975, 1977) who claim the isolation of enzymes capable of direct transfer of phosphate from inositol hexaphosphate to ADP as a means of energizing the early stages of the process of seed germination before the mitochondria become fully functional. If this system were to be proved general, then the involvement of phytic acid, the major storage form of phosphate in many seeds, is clearly much more important than merely as a substrate for phytase leading to the release of inositol and inorganic phosphate.

Storage of excessive inorganic phosphate in the vacuole or in a biochemically unavailable form in the cytoplasm is common to many crop species. The possibility exists that in crops raised in seed beds before being transplanted into permanent sites (e.g. rice, brassicas and horticultural species) a significant proportion of the total phosphate needs of the plant

could be provided in the first few weeks after germination. A combination of early feeding at luxury level followed by a foliar feeding at low levels could be useful in poor soils with high capacity for binding applied phosphate as a means of reducing the cost of fertilizer application.

REDISTRIBUTION OF PHOSPHATE WITHIN THE PLANT

Inorganic phosphate arriving at the leaf cells is esterified by both oxidative and photosynthetic phosphorylation. A continuous supply of phosphate from the roots is needed as leaf growth proceeds. Transfer between xylem and phloem occurs readily and considerable redistribution occurs between tissues and between root and shoot. Although recycling occurs, in times of shortage inorganic phosphate applied to leaves or roots is retained in the organ to which it is applied. Hormones play an important regulating role in this process, particularly in senescent plants in which young seeds are developing. The high concentrations of hormones characteristic of developing seeds appear to be concerned with the diversion of applied phosphate towards them (Seth & Wareing 1967). The relationship between the level of cytoplasmic phosphate and that of chloroplasts of leaf cells has received relatively little attention but is of great importance in the control of starch synthesis. Herold *et al.* (1976) have used the technique of mannose sequestration to prevent the interchange between cytoplasmic phosphate and the triose phosphate of the chloroplast thus causing a drop in starch synthesis. This effect appears to be characteristic of C_4 plants (i.e. which fix CO_2 into oxaloacetate) where the photosynthetic rate is reduced by mannose as a result of the prevention of the regeneration of phosphoenolpyruvate, the primary CO_2 acceptor. Deficiency of phosphate can also increase starch synthesis even though the photosynthetic rate is lowered. Observations of this type serve to amplify the importance of fine control of inorganic phosphate levels in the cytoplasm and re-examination of several aspects of phosphate nutrition would be profitable now that it is more widely appreciated that the general metabolic turnover in the cytoplasm is governed by a small fraction of the total cellular inorganic phosphate.

THE ROLE OF MICROORGANISMS IN THE USE OF OTHER FORMS OF PHOSPHATE

It must be firmly stated that the normal plant root is part of a system involving microorganisms both on the root surface and inside the cells. The vesicular-arbuscular mycorrhizas are a good example of a beneficial liaison between the higher plant root and a fungus and are probably the most

frequently encountered fungi in soil. They are more abundant in soils deficient in phosphate and can give rise to a significant increase in the rate of absorption by the host plant, primarily as a result of increased functional surface area. The results of Tinker & Sanders (1975) suggest that the fungus uses only the pool of exchangeable phosphate but less-readily available forms may be exploited in the correct conditions. Mineralization of insoluble phosphates such as apatite by bacteria and fungi is well known and the production of organic acid may be important in this respect although the amount of acid required is probably much greater than that actually secreted. The other major aspect of biological mineralization is that of hydrolysis of ester forms released during the breakdown of organic material of both plant and animal origin in the soil. Major attention has been given to the production of phosphatases at the root surface and their release into the rhizosphere. These enzymes hydrolyse sugar phosphates and include the phytase that breaks down phytic acid, the hexaphosphate of myo-inositol. Such phosphatases may originate in the root itself or be released by microorganisms. Clark & Brown (1974) compared two inbred strains of maize with widely-differing capacities for phosphate absorption. The higher capacity for absorption was correlated with a higher level of phosphatase on the root surface. The contribution to the total phosphate available to the plant brought about by microbial attack may be relatively small but the possible direct use of compounds such as inositol phosphates as phosphorylating agents referred to earlier may change views on the importance of these organic forms.

Some possible fertilizers of the phosphoryltriamide type appear to enter the plant passively and are distributed throughout the plant in the transpiration stream. Matzel (1976) has shown that most of these compounds are not readily hydrolysed but selection for crop varieties with hydrolytic ability is possible. If these compounds were readily hydrolysed in the soil they would offer no advantage over orthophosphate since when released the phosphate is fixed in the soil. Information on the metabolism of compounds of this type is needed particularly if they become attractive as low-bulk forms of phosphorus and nitrogen.

INTERACTIONS WITH OTHER ESSENTIAL NUTRIENTS

The efficiency of phosphate use depends on a fully-functional system and some insight into the mechanism by which the ion is metabolized can be gained by examination of the effects of other ions. Most of the effects of other elements such as nitrogen stem from the increase in growth, but changes in pH

TABLE 1

The effect of boron status on anion uptake in five-day-old plants of three species

Species	Rate of anion uptake $(nmol\,g^{-1}\,h^{-1})$	Boron status*			
		$B-$	$B-$ ($+10\mu M$-boric acid)	$B+$	$B+$ ($+10\mu M$-boric acid)
Maize	Cl^-	430	705	605	710
	$H_2PO_4^-$	66	171	116	190
Sunflower	Cl^-	690	1030	1300	
	$H_2PO_4^-$	70	105	103	
Field bean	Cl^-	190	230	480	
	$H_2PO_4^-$	52	118	112	134

Absorption by 1 cm root tips from $10\mu M$-$KH_2{}^{32}PO_4$ in $1mM$-$Ca(NO_3)_2$ labelled with ^{32}P at $0.10\,\mu Ci$ ml^{-1}.
* Boron deficiency ($B-$) was induced by omitting boron from the culture solution during the 4th and 5th day of growth. Boron was resupplied (as $10\mu M$-boric acid) 1 h before the measurement of phosphate and chloride uptake.

brought about by the absorption of ions by the release of protons can produce more rapid responses in phosphate absorption. More direct effects on the absorption process can be demonstrated with other elements such as calcium and boron. The specific role of boron is of particular interest because mild deficiency of this element causes a severe inhibition of phosphate absorption in root tips of many crop species. The capacity for phosphate absorption can be restored almost immediately by the addition of $10\mu M$-boric acid, a fact which implies that boron is needed for the process of transport across the membrane (Table 1). An important aspect first observed with maize is that plants of high boron status also respond to the addition of $10\mu M$-boric acid and this implies that these plants are operating at about two thirds of their maximal capacity and that the capacity of boron-deficient plants is reduced to about one third. In addition to phosphate other ions such as potassium and chloride respond to the presence and absence of boron and the activity of an associated membrane ATPase follows a similar pattern (Pollard *et al.* 1977). Investigation of the interaction between phosphate and other ions at the membrane level and at the stages involving metabolism is of obvious use in helping to elucidate the mechanisms involved in the absorption process.

DIFFERENCES IN THE USE OF PHOSPHATE BETWEEN AND WITHIN SPECIES

Reference has already been made to differences between inbred strains of maize in their capacity to absorb phosphate. Some species can complete their growth on soils in which the steady concentration of available phosphate is

too low for other species to survive. Capacities for absorption and transport vary widely and the genetic basis for these differences has received relatively little attention. Table 1 shows that the capacities for phosphate absorption by root tips are similar in the three species of similar age examined and that the responses to deficiency and resupply of boron are also similar. Comparison of cereals with legumes shows that the capacity for absorption is high in both species from an early stage of development. The ability to transport phosphate to the shoots of barley, oats and maize develops during the first few days after germination and increases steadily over the first month. In field beans and peas, however, the onset of this capacity for transport is delayed for 2–3 weeks and can be induced within 24 h at any stage by removal of the cotyledons (Loughman 1976). Few observations have been made on the effects of differences in species, varieties within species or seed size on the relative efficiency of absorption and transport and further work could help in devising economies of fertilizer use. Selected strains of white clover capable of improved growth on soils with low phosphate concentrations are being characterized with respect to several properties, e.g. densities of the root system, root hairs or mycorrhizas. Because of the relatively low diffusion rates of phosphate ions in soil (perhaps 0.1% of that in free solution) the development of the root system is of great importance in ensuring the most efficient association of the root surface with the maximum volume of soil solution. Although root hairs may be of minor importance in experiments carried out in water culture it is now accepted that greater importance must be attached to their role in soil where the process of diffusion to the root surface is likely to be limiting.

The results of a more detailed examination of the way in which species differ in their capacities for absorption and transport are shown in Fig. 4. The six species are of identical age but differ in size and their absorption rates range between 90 and 440 nmol g^{-1} h^{-1} on a dry weight basis.

The capacity for transport ranges from 1% in peas to 18–30% in the other species and the sensitivity of the systems to mannose also shows interesting differences, as already discussed (Table 2 and Fig. 3). The fact that young pea plants are so much less active as transporters although efficient at absorption confirms the earlier finding with field beans. The fact that deseeding activates the transport process in field beans implies that the presence of the seed inhibits transport and that the phosphate supply to the shoot comes from the seed. However, this is not the case in mung beans where the seed size relative to the plant is similar to that of peas and it seems that major differences in transport capacities do occur between species within the same family. Hormones are known to be important in the control of nutrient supply to seeds

TABLE 2

The effect of mannose on transport to the shoots of phosphate absorbed by the roots of six species

Time (hours)	Transport (%)											
	Maize (var. INRA 200)		Barley (var. Proctor)		Oats (var. Blenda)		Sunflower (var. Polestar)		Mung bean		Pea (var. Alaska)	
	Control	+Mannose	Control	+Mannose	Control	+Mannose	Control	+Mannose	Control	+Mannose	Control	+Mannose
1	3.90	0.68	6.89	0.38	6.96	0.52	5.53	3.34	3.50	1.90	0.24	0.68
2	5.72	1.32	12.13	0.44	20.62	0.36	10.77	4.08	11.49	3.64	0.62	0.33
4	18.50	1.50	30.13	0.49	29.53	0.47	23.59	14.64	19.93	19.28	0.07	1.17
7	39.16	0.76	21.19	0.82	35.32	0.39	45.54	31.00	37.45	20.26	4.54	1.47

12-day-old plants treated with $10\mu M$-$KH_2{}^{32}PO_4$ at pH 5.5 in the presence and absence of 1mM-mannose at 20 °C and 12 700 lx.
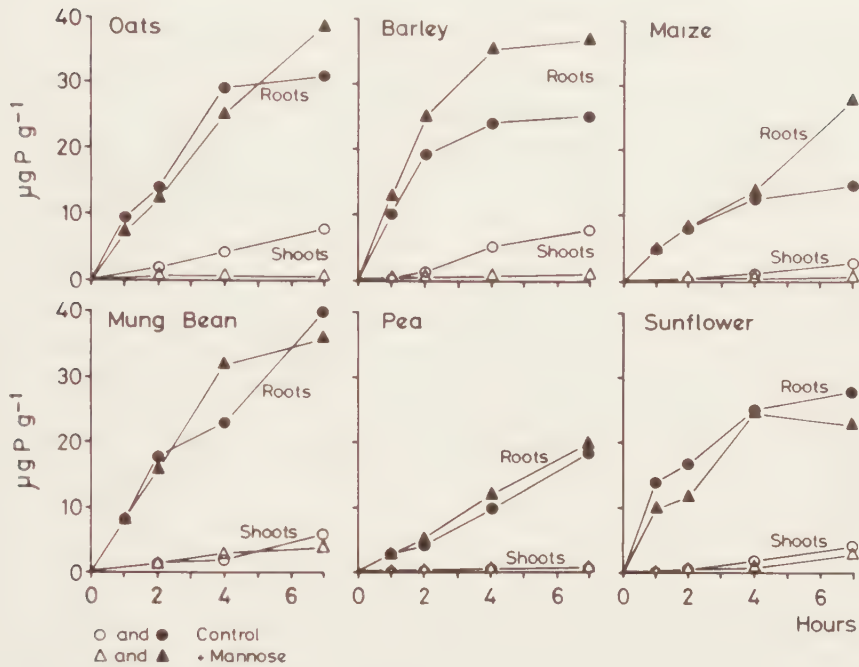
FIG. 4. The effect of mannose on the absorption and transport of phosphate by six species: 12-day-old plants were treated with $10\mu M$-$KH_2{}^{32}PO_4$ at pH 5.5 in the presence and absence of $1mM$-mannose at 20 °C and 12 700 lx.

and it would be interesting to establish whether the export of ions from seeds is also correlated with levels of specific hormones.

CONCLUSION

The importance of phosphate to plant growth is obvious and the provision of adequate amounts is essential for maximal crop response. If fertilizer costs increase and maximal economy of use of phosphate is to be achieved more information on the factors controlling its distribution in the soil and its use by the plant is necessary. In certain field conditions application through the leaves may be advantageous and both the positioning and timing of applied phosphate for root absorption will become of greater importance if supplies are limited. Major differences have been demonstrated in the capacities of

different species for both absorption and subsequent transport. In addition it is clear that although the capacity of roots to absorb phosphate is developed within hours of emergence of the radicle, the ability to transport recently acquired phosphate to the shoots may be delayed for weeks in some species. Much needs to be done to evaluate the importance of these differences to the economy of the plant and the modification of these mechanisms by changes in the internal and external environment demonstrated here might enable a more balanced view to be taken of the overall problem of phosphorus nutrition. Further work on selection of genotypes with increased capacities for absorption and transport is likely to produce useful material for soils where the available phosphate is low. Another important aspect related to crop performance is the relationship between the yield and the functional amount of orthophosphate in the plant. This functional component may differ from the total orthophosphate by more than a 100-fold and the importance of its contribution to the overall control of plant metabolism can hardly be overstressed.

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Discussion

Shaw: Wanĕk (1975) explained how some of the 'gold-plated' fertilizers, such as $PO(NH_2)_3$ (phosphoryltriamide) and the cyclic amides $[-P(NH_2)_2 = N-]_3$ and $[-P(NH_2)_2 = N-]_4$, could be taken up by oats in higher concentration (as measured with ^{32}P) than conventional fertilizers because they are neutral rather than ionic molecules. Wanĕk explained this by the lower osmotic pressure generated, which (he suggested) did less damage to the cells.

Loughman: We used some of these organic forms some years ago, specifically because they were neutral, to follow the movement of water in whole plants. It was assumed that they entered the plants in a physical way. If they are metabolized outside the root (which seems to be the case for some of them), they have no advantage because they behave as normal fertilizers but, if they can enter and are metabolized within the plant, they might be advantageously used on soils with a low phosphate concentration which bind phosphate firmly. Little is known about their metabolism although Matzel (1976) showed that they are not readily hydrolysed (see p. 163).

Tinker: Professor H. W. Woolhouse at Leeds concluded that phosphoamides are hydrolysed rapidly in soil and that the plants consequently take up only ordinary orthophosphate. But they were also hydrolysed by phosphatases on the root surface. So even in a non-soil environment the chance of these compounds passing into the plant unchanged is small.

Shaw: That does not explain the increased uptake that Wanĕk reported (1975). Could it be that, although the compounds are hydrolysed to orthophosphate, they are more readily available in the soil at the surface of the plant?

Tinker: I assume that they are not so strongly adsorbed as orthophosphate, in which case they could be more available. Has the adsorption isotherm been determined in soil?

Shaw: Waněk has done some adsorption and diffusion studies (1975).

Loughman: Neutral molecules face less of an adsorption problem.

Tinker: Many agricultural chemicals (e.g. herbicides) are neutral but are still strongly adsorbed on the organic matter in the soil. The fact that it is neutral does not rule out adsorption.

Kabbaj: Usually phosphate is applied to soil as calcium phosphate and sometimes ammonium phosphate, but rarely as potassium phosphate. Why did you use potassium phosphate in your culture solutions?

Loughman: We normally added calcium ions to our experimental system because otherwise we would be using a deranged system; calcium is vital for membrane integrity. We have used different ions as well as culture solution but we find the same pattern of phosphorylation.

Tinker: The vesicular-arbuscular mycorrhizas you mentioned (p. 162) infect most of the world's vegetation. Most of the phosphorus that enters vegetation probably does so, not directly through the surface of the root, but first through the fungal hypha from where it is then transferred. We are now sure that a large fraction of the phosphate initially taken up by the fungus is converted into polyphosphate which is segregated in the small vacuoles of these fungi. Phosphorus is then probably transported by cytoplasmic streaming as little packages of polyphosphate. We do not yet know whether the polyphosphate is hydrolysed back to orthophosphate before being handed over to the host.

Loughman: It seems that inorganic orthophosphate is transferred (Harley & Loughman 1963), even though there had been phosphorylation within the fungus. In our system we observed movement of orthophosphate through the sheath into the core of the root where it was metabolized.

Shaw: Are these polyphosphates inorganic or organic?

Tinker: They are inorganic, consisting of as many as 200 units.

Shaw: Do cyclic polyphosphates participate?

Tinker: The identification of these polyphosphates is based on gel electrophoresis so far and indicates about 200 units, but we don't know whether the structure is cyclic.

Loughman: Pyrophosphatases are active in several of these systems, so if polyphosphate is the storage form inorganic pyrophosphatases may liberate the orthophosphate in the right circumstances.

Emsley: How does borate affect the transport of phosphate across the membrane?

Loughman: Its specific effect on membrane transfer is probably the only metabolic effect of boron that does not involve growth – most responses to boron are long-term.

The rate of uptake of phosphate in a boron-deficient maize plant is about half that in a boron-sufficient plant (Pollard *et al.* 1977). Addition of 10μM-boric acid to the boron-deficient plant restores the rate of phosphate uptake. We routinely used 30 min pre-treatment but in certain circumstances one can restore the rate of phosphate uptake instantaneously. As boron deficiency develops, ATPase activity in the plasmalemma falls and when ion uptake is restored so is the ATPase activity. That also applies to the magnesium-activated uptake of potassium and rubidium ions; uptake is restored as boron deficiency is rectified. Results of our most recent experiments suggest that the ATPase on the plant plasmalemma transports potassium in. In animals both potassium uptake and ATPase activity can be blocked specifically with ouabain, but plants do not respond to ouabain. The effect of boron deficiency is clearly similar to the effect of ouabain on animal tissues.

Shaw: Boric acid forms chelating complexes with diols. Is it possible that boric acid by chelating helps the sugar phosphate?

Loughman: The concentrations of boron are so low: in plants about 0.1 mmol/l. The boron appears to be bound in the membrane and could transport neutral sugars or sugar phosphate in addition to inorganic phosphate. When we isolated membranes from boron-deficient plants, we found half as much boron in the membranes as we did in normal plants (unpublished results).

Shaw: This means that the phosphate is transferred across the membrane in some combination with boric acid and this complex then breaks down.

Loughman: That is possible; unfortunately, few people are working on boron metabolism and phosphate uptake in plants (although many groups are studying potassium and chloride entry, even though these ions are not meta-bolized) and we do not yet know what the mechanism is.

Kirby: You implied that a plant will take up phosphate faster than the phosphate will diffuse to it. Is this true in your conditions and in steady-state conditions?

Loughman: I was referring to the soil. Studies on depletion zones around the root confirm this.

Tinker: A soil could be supplied with phosphate to such a level that the concentration in the depletion zone remains high relative to the initial con-centration. But the statement is true in most circumstances.

Kirby: But I presume it would not be true for Dr Loughman's solutions otherwise some odd conclusions follow.

Loughman: In the experimental solutions that would be less of a diffusion problem compared to soil solution; it is difficult to provide adequate stirring of the surface layers.

Larsen: I support your philosophy of selecting varieties that can better use the available phosphate and perhaps other nutrients. In the past we have been supplying nutrients to the varieties we were breeding. Now, perhaps the time has come to turn it the other way round and try to breed varieties that would thrive on the nutrients present. Can our studies of the pathways of phosphorus help in this respect?

Loughman: In these inbred maize strains the capacity for phosphate uptake and the capacity to survive on a low phosphate soil correlate significantly with the activity of surface phosphatases (Clark & Brown 1974). We are at present looking for other mechanistic differences (as I suspect there might be). So far four strains have been isolated that show these much increased capacities for uptake.

Larsen: Nielsen & Barber (1978) have investigated different varieties of maize with regard to their ability to absorb phosphate and found a three-fold difference in both water culture and in field experiments.

Loughman: The species difference seems not to have been noticed before and there are significant differences in the mechanism of phosphate use between species. The reversal of the mannose effect (Fig. 3) may have considerable implications for assessment of metabolic differences within the root.

R. J. P. Williams: If the fungus limits the entry of phosphate into the plant, why not breed the fungus rather than the plant?

Larsen: Some researchers have done precisely that, e.g. Barbara Mosse at Rothamsted and Lynette Abbott at the University of Western Australia.

Tinker: Nobody is yet sure whether mycorrhizas control phosphate uptake in the field. Maize, for instance, easily becomes heavily infected and, certainly in controlled conditions, enormous yield responses can be observed. But in the soil in fields, nobody yet knows what the true effect of the fungus is.

Whether or not the fungus is involved, if diffusion (i.e. the rate at which phosphorus can get to the roots) rather than the root-uptake properties are limiting, then even the development of a more efficient root (with, say, more uptake sites or uptake sites with a different K_m and so on) does not matter much, because, as far as one can tell, most of the plant roots existing at present are (to judge from the usual Michaelis–Menten type of uptake curve) efficient even at concentrations of 10 nmol/l. The roots can thus take up phosphate from extremely dilute solutions. Now if that is true, the limitation on the uptake rate is outside the root and the problem becomes one of soil and root geometry, and not a physiological one.

Loughman: Once the phosphate is in the root the transport capacity can be low (as I showed for field beans) and may not develop for some weeks. This capacity, too, varies within species.

R. J. P. Williams: I am still not clear about what limits the phosphate getting to the plant. I gather that diffusion is important—that the plant takes up phosphorus faster than the phosphorus reaches it—but then it seems that microbes rather than plants are limiting. Am I right that people should be trying to breed plants with healthy and extensive roots, irrespective of whether the roots are covered with fungi?

Larsen: Yes; and also roots with a long, active life.

Loughman: . . .and many root hairs.

Larsen: There are different types of microbes; most plants have mycorrhizas but sugar beet is an important exception.

Loughman: But they do have bacteria and other fungi.

R. J. P. Williams: If the phosphate, having overcome the limitation of diffusion to the root surface. is trapped as polyphosphate. is there another limitation on incorporation of phosphate which we do not know about?

Larsen: Water culture—hydroponics, which is at present in fashion—eliminates the diffusion factor, so clearly there is another limiting factor.

Loughman: The efficiency of the uptake mechanism is high, apparently with esterification as an integral part of the transfer. I may quote one experiment. Even at 0 °C plants take up phosphorus and, even though esterification is reduced to a third of its normal value, phosphorylation continues. In some storage tissues (e.g. potato slices, which have relatively low metabolic activity) the esterification can be stopped at 0 °C; labelling experiments show that the tissue takes up a little [^{32}P]orthophosphate but does not use it for esterification although on transfer at 20 °C the orthophosphate is rapidly used to make esters. That is the only experimental evidence that I know of for transport of orthophosphate as such across the membrane. In other tissues the rate of esterification is so fast that the uptake process may be the esterification step of oxidative phosphorylation. Whether that membrane is the plasmalemma or the mitochondria, or whether in these conditions the plasmalemma is an energy-transducing membrane is another matter.

Pirie: Although you claimed that lowered oxygen levels (1–2%) inhibited transport, most C_3 plants (which fix CO_2 by way of phosphoglyceric acid) appear to grow *better* in 2% than in 21% oxygen. If they can transport phosphate, how do they manage that?

Loughman: In 2% oxygen the transport upwards to the shoot was reduced (but not to zero) whereas the entry into the roots was normal.

Pirie: You haven't answered my question. Why do plants like barley, C_3

plants, prefer 2% oxygen to atmospheric oxygen? Maybe they don't like living in their own muck!

Shaw: You mentioned that different species of plant responded differently. Did they differ in uptake or in transport or in both?

Loughman: Uptake capacities, metabolic capacities and transport capacities all differ. For instance, the rate of uptake (per g of root tissue) varies over a five-fold range. The capacity for transport differs more: over 4–5 h 12-day-old pea plants transport only 1% but sunflower and other species transport 30% of what they take up.

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Phosphorus cycles of forest and upland grassland ecosystems and some effects of land management practices

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Abstract The distribution of phosphorus capital and net annual transfers of phosphorus between the major components of two unfertilized phosphorus-deficient UK ecosystems, an oak—ash woodland in the Lake District and an *Agrostis-Festuca* grassland in Snowdonia (both on acid brown-earth soils), have been estimated in terms of kg P ha^{-1}. In both ecosystems less than 3% of the phosphorus, totalling 1890 kg P ha^{-1} and 3040 kg P ha^{-1} for the woodland and grassland, respectively, is contained in the living biomass and half that is below ground level. Nearly all the phosphorus is in the soil matrix. Although the biomass phosphorus is mostly in the vegetation, the soil fauna and microorganisms contain significant quantities. Turnover through the woodland vegetation is slower (25%) than in the grassland vegetation (208%). More than 85% of the net annual vegetation uptake of phosphorus from the soil is returned to the soil, mainly in organic debris, which in the grassland ecosystem is more than twice as rich in phosphorus (0.125% P) as in the woodland ecosystem (0.053% P). These concentrations are related to the rates of turnover (input/P content) of phosphorus in the litter layer on the soil surface; it is faster in the grassland (460%) than in the woodland (144%). In both cycles plant uptake of phosphorus largely depends on the release of phosphorus through decomposition of the organic matter returned to soil. In both the woodland and the grassland, the amount of cycling phosphorus is potentially reduced by its immobilization in tree and sheep production and in undecomposed organic matter accumulating in soil. It is assumed that the reductions are counterbalanced by the replenishment of cycling phosphorus by (i) some mineralization of organically bound phosphorus in the mineral soil, (ii) the income in rainfall and aerosols not being effectively lost in soil drainage waters and (iii) rock weathering.

The effects of the growth of conifers and sheep grazing on the balance between decomposition and accumulation of organic matter returned to soil are considered in relation to the rate of phosphorus cycling and the pedogenetic changes in soil phosphorus condition leading to reduced fertility. Although controlled sheep grazing speeds up phosphorus cycling and may reverse the pedogenetic trend in favour of soil improvement, conifers may slow down phosphorus cycling and promote the pedogenetic trend towards infertility.

Various attempts have been made to draw up phosphorus budgets for forest and agricultural ecosystems and to use the information to assess the impacts of land management practices on the phosphorus capital and, therefore, the fertility of ecosystems (see Cooke 1967). So far, these budgets have mostly taken the form of balance sheets indicating the relationships between net inputs of phosphorus from natural sources and fertilizers and net losses by soil-leaching processes and cropping. Although such an approach can provide a preliminary basis for assessment (Newbould & Floate 1978), it does not provide any insight into the effects of management on the biological cycling and, therefore, the state of the phosphorus capital within the eco-system. The latter factors, in addition to net gains or losses by the system as a whole, may also affect the long-term fertility of the site, particularly where soils are poor and infrequently fertilized.

Although the individual pathways of phosphorus cycling are well known and there are data on the quantities present in and transferred between the components of some (mainly forest and grassland) ecosystems, there are, unfortunately, still few integrated studies which interrelate the quantities of phosphorus cycling through components of single whole ecosystems. Con-sequently, comparisons of phosphorus cycles and the effects of management can as yet only be superficial.

As part of the International Biological Programme, detailed studies have been made of a semi-natural woodland, Meathop Wood, in the Lake District of the UK (Satchell 1971) and an upland pasture in Snowdonia (Heal & Perkins 1978). I shall describe the phosphorus cycles of these two unfertilized ecosystems and compare some key features of the cycles. I shall also discuss the effects of conifer plantations and sheep grazing on phosphorus cycling and soil phosphorus changes during soil formation (pedogenesis).

MEATHOP WOOD

This semi-natural woodland, just above sea level in the Southern Lake District with an annual rainfall of 120 cm and a mean annual temperature of 7.8 °C, is a mixed deciduous hazel coppice with standards, dominated by oak, ash, birch and sycamore. As far as is known the site has carried woodland continuously and has a history of coppicing and charcoal-burning manage-ment dating from at least the 16th century. As timber was last removed in 1939, the woodland is now only just returning to the closed-canopy stage in development. The soil, highly phosphate-fixing and with pH 4.7, is a brown earth derived mainly from Silurian slate and shale drift overlying Carboni-ferous limestone. Plant productivity in the woodland is limited by

phosphorus supply, as plants grown in the soil in pots produce marked increases in growth (up to 700%) when phosphate fertilizer is applied.

The phosphorus capital within the site, to a soil depth of 50 cm, totals about 1890 kg ha^{-1}; 97% of the phosphorus is in the soil, with 840 kg P ha^{-1} in stones and 995 kg P ha^{-1} associated with the fraction of soil that will pass through a 2-mm sieve. Only 2.6% is in the living biomass (Fig. 1); 45 kg P ha^{-1} is
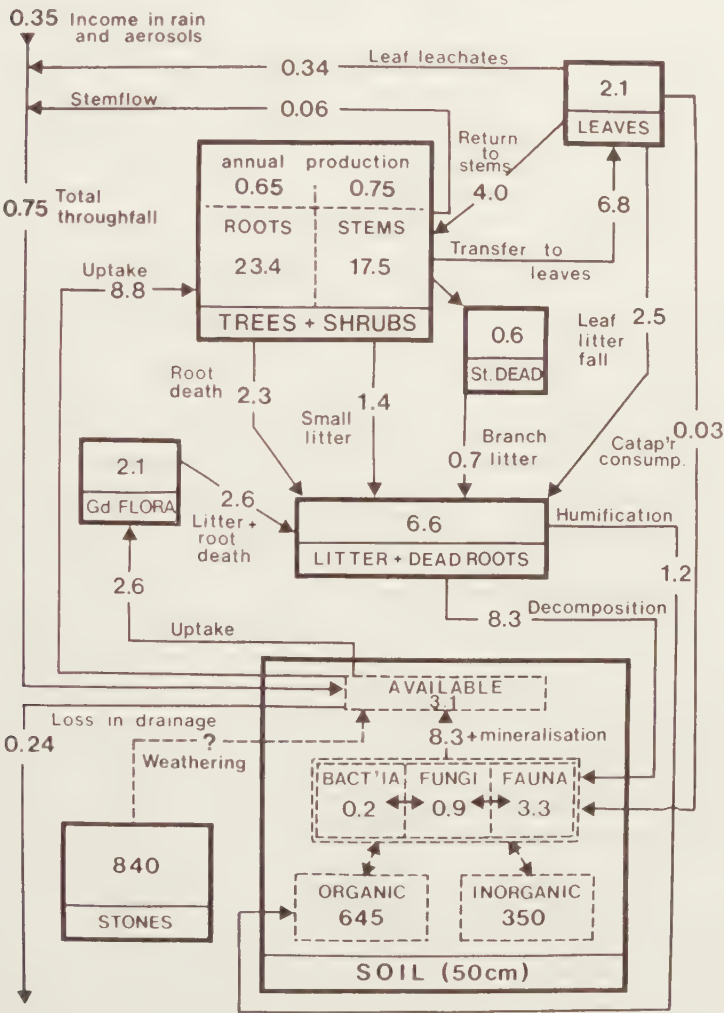
FIG. 1. Phosphorus cycle of a mixed-deciduous woodland (Meathop Wood, Cumbria, UK): contents are given in kg P ha^{-1}; transfers in kg P ha^{-1} yr^{-1}. St. = standing; Gd. = ground; Catap'r = caterpillar, Bact'ia = bacteria.

contained in living trees, shrubs and ground flora and 4.4 kg P ha^{-1} in living fauna and microorganism populations.

The trees and shrubs together take up a minimum of 8.8 kg P ha^{-1} yr^{-1} from the soil, of which 1.4 kg P ha^{-1} yr^{-1} is retained in the wood production of both stems and root systems. Most of this uptake (80%) is returned to the soil in leaf, twig, branch and small litter, leaf and stem leachates and by root death. The return in leaf litter is only 35% of that present in leaves in the middle of summer, for trees withdraw some 4 kg P ha^{-1} from the leaves before 'leaf fall' (the main autumnal fall of leaves) to conserve their capital. The quantity returned to soil annually from above-ground sources is about 25% of that contained in stems and canopy, while the annual return to soil by death of roots, roughly equivalent to that returned by leaf fall, is only about 10% of the total contained in the root-system component.

Additional phosphorus is lost from root systems to soil in exudates but this loss has not been investigated. Some idea of the importance of this pathway can be gained from the exudation rate from roots of established trees (0.075 µg P [mg root]$^{-1}$ [14 d]$^{-1}$; W. H. Smith, personal communication). Assuming that root exudation in Meathop Wood takes place in the six spring and summer months only and from the unsuberized roots less than 2 mm in diameter (which amount to 3% of the total root biomass), I estimate that exudation losses to the soil are about 2 kg P ha^{-1} yr^{-1}. This is equivalent to the amount returned to soil from leaf-litter or by root death. That this is the major transfer pathway between trees and soil is also suggested by the work of Rakhteyenko (1958) and Woods (1970), who have shown rapid and substantial transfer of ^{32}P from roots to soil. The ground flora takes up a minimum of 2.6 kg P ha^{-1} yr^{-1} from the soil and returns this to soil by root death and leaf litter. There are also returns from ground flora in leaf leachates and root exudates but these have not been quantified.

In addition to plant uptake, up to 10 kg P ha^{-1} yr^{-1} may be directly but temporarily immobilized in forest soils by microorganisms (Ausmus *et al.* 1976), but microbial immobilization in Meathop soils will be small because there is insufficient energy available for much microbial growth (Gray & Williams 1971).

The amount of available phosphorus in the soil is low, about 3 kg P ha^{-1}, so the phosphorus uptake by the vegetation, at least 11.4 kg P ha^{-1} yr^{-1}, depends heavily on the cycling by soil fauna and microorganisms of phosphorus returned to the soil in organic debris. This dependence is a common feature of forest ecosystems (Ovington 1962; Johnson & Risser 1974; Switzer & Nelson 1972). The importance of cycling from litter is demonstrated by the observation that removal of litter from forests reduces subsequent growth of trees

(Jemison 1943; Baule & Fricker 1970) although it takes other nutrients besides phosphorus from the site.

Some of the organic matter returned annually to soil (perhaps as much as 25%) does not decompose but accumulates in the profile (Duvigneaud & Denaeyer-de Smet 1970; Van der Drift 1971), immobilizing some phosphorus. About 65% of the phosphorus in the fraction of soil smaller than 2 mm (i.e. 35% of the phosphorus in the whole soil profile, including stones) is already bound in organic forms. Based on the figure for the accumulation of organic matter in Meathop soil of 2930 kg ha^{-1} yr^{-1} (Satchell 1971), about 1.2 kg ha^{-1} yr^{-1} of phosphorus may be added to the soil in this way. As a small amount of organically-bound phosphorus may be mineralized within the soil profile it is not certain that there is a net accumulation of organic phosphorus. However, conversion of phosphorus into organic forms, making it relatively unavailable for recycling, is a natural process in soil development (Floate 1962; Walker 1965) and mean accumulation rates of 2.3 and 5.6 kg organic P ha^{-1} yr^{-1} during the establishment of woodland on arable soil left uncultivated for 83 years have been recorded (Jenkinson 1971). Thus an accumulation rate of 1.2 kg P ha^{-1} yr^{-1}, representing an annual conversion of 0.065% of the total soil profile phosphorus into organic forms, appears a plausible estimate.

Immobilization of phosphorus in organic soil matter, in addition to the retention of 1.4 kg P ha^{-1} yr^{-1} in tree production, will significantly reduce the quantity and rate of phosphorus cycling, unless there is some replenishment. One possible source of the 0.35 kg P ha^{-1} yr^{-1} is in the rainfall and aerosols but this input is hardly significant, when the estimated loss of 0.24 kg P ha^{-1} yr^{-1} due to leaching of the soil profile is taken into account. Another possible source is the uptake by tree roots from lower soil horizons (Goldschmidt 1934; Hartmann 1967), but this may not be important in Meathop Wood as only 1–5% of the tree roots penetrate deeper than 50 cm. A further source is the weathering of rock minerals. Klausing (1956) considered that weathering rates of 1.2 and 2.1 mm yr^{-1} for granite and diorite, respectively, under beech forest significantly enriched soils with phosphorus and thereby enhanced its cycling. Sweeting (1966) had indicated that the rate of weathering of limestone is about 40 mm (1000 yr)$^{-1}$, which could result in erosion of 1040 kg limestone ha^{-1} yr^{-1} (D. F. Ball & J. E. Satchell, personal communication). As the limestone, however, is rather pure and contains only 0.003% phosphorus, only 0.03 kg P ha^{-1} yr^{-1} could originate from this source. The most likely source is therefore apatite in the slate and shale stone material (D. F. Ball & J. E. Satchell, personal communication) but the weathering rates of these materials are unknown. For Meathop Wood it is assumed that reductions in the amount of phosphorus in cycle due to immobilization are just being replenished by a combination of these mechanisms.
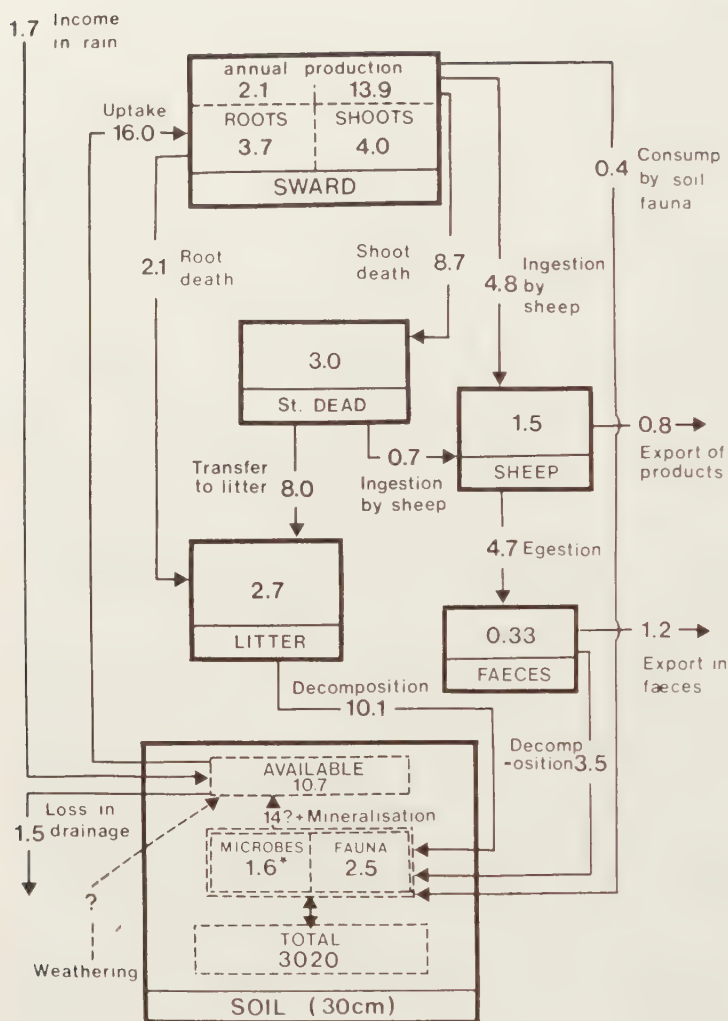
FIG. 2. Phosphorus cycle of an *Agrostis–Festuca* grassland (Llyn Llydaw, Snowdonia, UK): contents in kg P ha⁻¹; transfers in kg P ha⁻¹ yr⁻¹ (based on Perkins 1978) ˣ Data are for the *Agrostis–Festuca* grassland at Moor House (O. W. Heal, personal communication, 1977).

SNOWDONIA GRASSLAND

This grassland ecosystem (Perkins 1978), elevated at 500 m in Snowdonia with an annual rainfall of 380 cm and a mean annual temperature of 7.2 °C, is dominated by *Agrostis tenuis* and *Festuca ovina*. The growth of the sward is

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largely governed by sheep grazing (12.5 animals ha^{-1}) from April to October. The site has been under similar management for some centuries. The soil, as in Meathop Wood a brown earth with pH 4.7, is derived from pumice tuff. The availability of phosphorus in the soil also appears to be limiting plant production (Perkins 1978).

As with the woodland ecosystem, only a small proportion (0.5%) of the total ecosystem phosphorus capital (3040 kg P ha^{-1}) is in the living biomass and about half of this is underground (Fig. 2). The living vegetation contains about 7.7 kg P ha^{-1}, and an estimated 4 kg P ha^{-1} is in soil fauna and microorganisms, the latter being more than in the sheep (1.5 kg P ha^{-1}). A further 5.7 kg P ha^{-1} occurs in standing dead grass and litter.

The annual plant uptake of phosphorus (16 kg P ha^{-1} yr^{-1}) and the amount returned to soil in plant litter and sheep faeces and by root death in the grassland (14 kg P ha^{-1} yr^{-1}) are higher than in the woodland. The annual return to soil by root death represents 60% of that in the standing biomass of grass roots, but the amount returned in leaf litter (8.7 kg P ha^{-1}) is over 200% of that in the above-ground standing biomass. When the sheep consumption of above-ground grass production of phosphorus (40%) is taken into account, the annual return to soil of phosphorus from leaf material is over 300% of that in the above-ground standing biomass. The amount of available phosphorus in the soil is lower than annual plant uptake and is probably replenished largely by decomposition of organic debris returned to soil.

As with the woodland ecosystem, a small proportion of the organic debris returned to soil probably does not decompose but accumulates in the soil profile (Kajak 1974). With the accumulation of organic matter some of the phosphorus in cycle is immobilized possibly lowering the amount of phosphorus available to the soil (White *et al.* 1976) but the annual rate of organic accumulation has not been estimated for Llyn Llydaw. However, the 0.2–12.5% higher organic phosphorus content of soils under more intensive grazing compared with that of soils under less intensive grazing has been attributed to the accumulation of phosphorus from faeces, which resist mineralization (Floate 1973 and personal communication, 1977). The organically bound phosphorus probably forms a high proportion of the total phosphorus content in the 2-mm soil fraction but is probably less than the 60–80% found for other upland grasslands (Floate 1970*b* and personal communication, 1977) as the organic matter content of the soil profile is considerably less (Perkins 1978).

As well as reductions in cycling phosphorus by the accumulation of organic matter, some 1.2 kg P ha^{-1} yr^{-1} is lost in faeces excreted on lower ground to which the sheep move at night. The transfer of phosphorus by sheep from one

area to another has been found elsewhere (Gillingham & During 1973). Also, 0.8 kg P ha^{-1} is removed in sheep products (meat and wool). These losses are probably counterbalanced by the excess of rainfall input over losses due to soil-profile leaching, some mineralization of organically bound phosphorus in the mineral soil and by rock weathering (Fig. 2). The high annual input of phosphorus in rainfall and outflow in profile drainage, compared to the woodland ecosystem, are due to the comparatively high rainfall in the Snow-donia area.

COMPARISON OF THE WOODLAND AND GRASSLAND CYCLES

(1) In both ecosystems continued uptake of phosphorus by plants depends largely on the recycling of phosphorus returned to soil in organic matter.

(2) The amount of cycling phosphorus is potentially reduced in the woodland by its immobilization by growing trees and in organic matter accumulated in the mineral soil, and in the grassland by its immobilization in sheep production (with subsequent 'export'), excretion in sheep faeces deposited elsewhere and possibly in organic matter accumulating in the mineral soil. It is assumed that cycling phosphorus is replenished by the natural mechanisms discussed.

(3) In both cycles the amount of litter on the soil surface and the quantity of phosphorus it contains remain approximately constant from year to year.

(4) The rate of phosphorus cycling is faster in the grassland than in the woodland ecosystem. This is demonstrated by the fact that (i) 208% more phosphorus is used in the grassland for plant production than is in the plant biomass (compared with the corresponding value of 25% for the woodland ecosystem) and (ii) the amount of phosphorus returned annually to the soil in the grassland is 460% higher than that in the standing litter and faecal material, whereas the corresponding value for the woodland is 144%.

(5) More organic matter is produced per unit P used in the woodland (2180 kg organic matter/kg P uptake) than in the grassland (939 kg/kg P uptake). Similar values have been found for other woodland and grassland ecosystems (Duvigneaud & Denaeyer-de Smet 1970; for Moor House, O. W. Heal, personal communication, 1977; Floate 1970b). Consequently the organic matter returned to soil in the grassland ecosystem is, overall, more than twice as rich in phosphorus (0.125% P, C/P 400) than that returned to soil in woodland (0.053% P, C/P 940). The litter layer on the soil surface of the grassland is also twice as rich in phosphorus as that in the woodland; grassland litter (0.086% P, C/P 590); woodland litter (0.049% P, C/P 1020). These values are related to the speed of phosphorus turnover through the litter layer and its consequent

rate of recycling and to the carbon/phosphorus (C/P) ratios in the soil profiles: Meathop Wood 84, Snowdonia Grassland 39. (I shall discuss the significance of the latter point later.)

The phosphorus cycle of the woodland is broadly typical of many temperate forest ecosystems. The quantities of phosphorus in the components and in the annual transfers between them are slightly higher than those for another oak woodland in the Lake District but similar to those for some forests elsewhere (Brown 1974; Duvigneaud & Denaeyer-de Smet 1970; Johnson & Risser 1974) and appear to be in the middle of the ranges of values reported for temperate forest ecosystems. Though the upland grassland phosphorus cycle is similar in form to those of other hill-pasture ecosystems, the quantities of phosphorus in some components, particularly the soil, and amounts in the annual transfers are somewhat higher than those for which data are available (Newbould & Floate 1978; Rehder 1976; for Moor House, O. W. Heal, personal communication, 1977). Some or all of these aspects of the phosphorus cycles in these two ecosystems may apply to other forest and upland grassland ecosystems.

SOME EFFECTS OF AFFORESTATION AND SHEEP GRAZING ON THE PHOSPHORUS CYCLE

The most important feature of the phosphorus cycles in both ecosystems is the dependence of plant uptake of phosphorus on the release of phosphorus from organic debris returned to soil. In upland areas of Britain, where climate (low temperature and high rainfall) tends to make the organic cycle slow (Crompton 1958), the slow release of phosphorus from returned organic matter is probably a major factor in the phosphorus deficiency that is common in these soils (Reith 1973; Mackenzie 1974; Newbould 1975). Management factors which directly or indirectly affect the balance between accumulation and decomposition of organic matter will also influence the cycling of phosphorus.

Afforestation

In the past four decades large areas of upland have been planted with monoculture coniferous forest, particularly spruce and pine species. Under such species tree litters accumulate on the soil surface (see Fig. 3) since production is faster than decomposition. This accumulation immobilizes phosphorus, sometimes in excess of 40 kg P ha^{-1} (Ovington & Madgwick

1959; Nykvist 1974; Moore & Norris 1974; M. Carey, personal communication, 1977), not including phosphorus which may have accumulated in the humus beneath the litter. The quantities of phosphorus immobilized in litter may vary with soil type; for example, almost twice as much accumulates in litter layers under spruce on peaty gleys compared with surface-water gleys (Adams & Dickson 1973). Also slightly more phosphorus may be immobilized in greater amounts of accumulated litter under poorly-growing trees than under trees that are growing well (Adams & Dickson 1973). Thus the C/P ratio of litter, usually much higher under conifers than hardwoods (Ausmus *et al.* 1976), increases under poorer trees, reducing the likelihood of the phosphorus recycling. Unless there is some compensation in the cycle either through an increased availability of phosphorus in the soil, additional uptake by roots exploring a larger volume of soil, or an increase in rock weathering, such large accumulations in litter reduce the rates of cycling of phosphorus, and, on the poorer sites at least, could potentially reduce tree growth.

Applications of lime while the trees are growing may favourably affect decomposition (Lohwasser 1953) but may sometimes only increase the amount of litter accumulated, without affecting the quantity of phosphorus

FIG. 3. View of soil surface under a 40-year-old sitka spruce plantation, showing accumulations of needle and branch litter.

immobilized (Adams & Dickson 1973), thus further increasing the C/P ratio and reducing the possibility of recycling. Lime may also adversely affect the nutrition of Sitka spruce (Adams & Dickson 1973). Phosphate fertilizer, when applied alone or with nitrogen and potassium fertilizer, releases the uptake of phosphorus by trees from its dependence on natural cycling processes until the phosphorus is fixed by mineral soil (Larsen & Probert 1968; Blanchet *et al.* 1971) or remain in the litter accumulated (Adams & Dickson 1973).

Litter accumulation naturally tends to reach its peak sometime after the thicket stage in tree growth (20–30 yr) and thereafter to decline slowly as trees mature (although the 'A₂' horizon continues to increase; Page 1968), indicating continued accumulation of organic matter in the soil profile and a retention of phosphorus in organic forms. However, changes in the microclimate and soil disturbance brought about by clear-felling (at 40–60 yr) may temporarily accelerate litter decomposition and result in some 20–30% of the immobilized phosphorus being mineralized (Nykvist 1974). It is probably this release of phosphorus (and other nutrients) that gives rise to the increased losses due to leaching from the soil profile (Bormann *et al.* 1974) and is responsible for enhanced second-rotation tree growth (Page 1974). The failure of second-rotation trees has been attributed elsewhere to a slow release of nutrients from accumulated litter (Florence & Lamb 1970). These observations do not necessarily conflict, for subsequent tree crops will probably give a range of responses on account of differences in site quality and management factors, such as whether fertilizer has been previously applied and, if so, how much. Much of the phosphorus immobilized in the accumulated organic matter under plantations, however, still remains so several years after clear-felling and replanting (Nykvist 1974).

Grazing

Many upland grassland soils, particularly under *Nardus* grass, are also characterized by a surface layer or mat ('A₀' horizon) of partially-decomposed plant material (Fig. 4) and its presence indicates slow decomposition (Floate 1970*b*). This mat is mainly derived from herbage neglected by grazing animals. Usually less than 30% of the grass produced is eaten (Floate 1970*a,b*) because stocking levels on hill land are low, being controlled exclusively by the number of breeding animals which can be kept over winter on the better pastures (Welch 1968; Williams 1973). The amounts of phosphorus immobilized in these mats can also be substantial—up to 50–60 kg P ha⁻¹ (Floate 1970*b*)—and, as with the forest ecosystem, this accumulation leads to inefficient phosphorus cycling (Floate *et al.* 1973). The thickness of the mat

Fig. 4. View of a soil profile under an upland grassland, the sward being transitional between one dominated by *Festuca–Agrostis* and one dominated by *Nardus*, showing an accumulation layer of partially decomposed plant litter.

can be reduced by increased grazing intensity (Floate 1970*b*) because some of the mat and an increased proportion of herbage is consumed and returned to the soil as faeces. Although the amount of phosphorus accumulated in the thinner mat is only slightly reduced, the C/P ratio of the mat is substantially lowered (Floate 1970*b*), leading to an increase in the rate of phosphorus turnover and phosphorus availability in the soil (Johnson *et al.* 1971). Some of the phosphorus in plant material consumed by sheep may also be mineralized when passing through the guts of animals, and phosphorus in the faeces, once on the soil surface, may mineralize faster than phosphorus in plant material (Floate *et al.* 1970*a*). In addition, intensified but controlled grazing with applied nitrogen–phosphorus–potassium fertilizers plus lime mobilizes phosphorus in the mineral soil (Floate *et al.* 1973). By these mechanisms intensified but controlled sheep grazing may stimulate phosphorus cycling rates up to 10 times and so increase sward productivity (Floate *et al.* 1973).
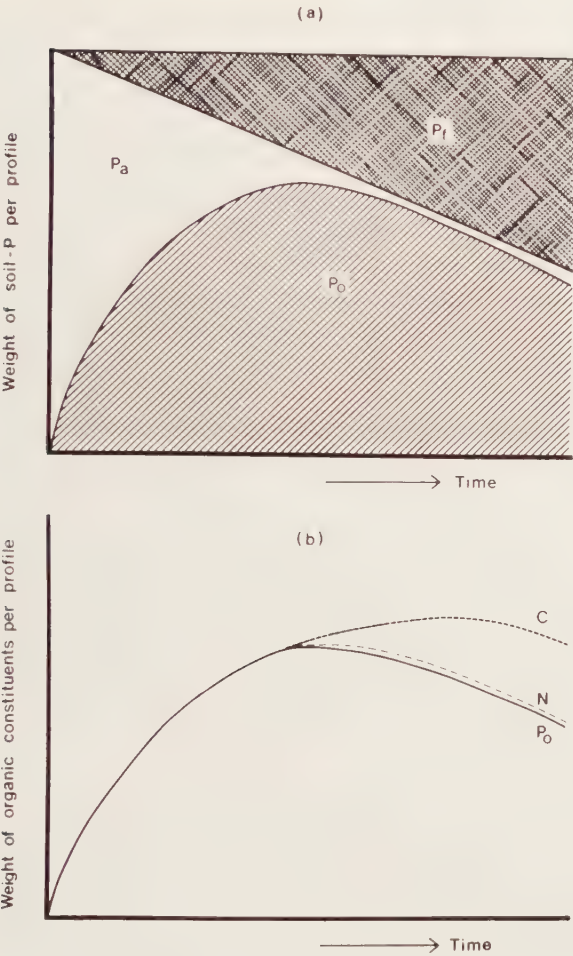
FIG. 5. Changes in the forms of (a) soil phosphorus and (b) constituents of soil organic matter during soil development (after Floate 1962 and Walker 1965) (redrawn from Floate 1970b): P_f, inorganic phosphorus insoluble in $2M$-H_2SO_4 (fixed-iron and Al bound); P_a, inorganic phosphorus soluble in $2M$-H_2SO_4 (soluble-iron, aluminium, calcium and apatite bound); P_o, organic phosphorus; C, carbon: N, nitrogen.

PEDOGENETIC CHANGES IN THE FORMS OF PHOSPHORUS IN SOIL

As a result of mineral weathering, leaching and long-term accumulation of organic matter during pedogenesis (soil development), the forms in which

phosphorus occurs in the soil profile change (Fig. 5) and these changes at later stages reduce soil fertility (Wells & Saunders 1960; Floate 1962; Walker 1965). The effects of management of land under grassland or forest may have different influences on these changes. The stimulation of phosphorus cycling by intensifying grazing pressure is associated with reductions in the C/P (from 132 to 96) and carbon/organic phosphorus (C/P_o) ratios (from 254 tot 161) in soil profiles (Floate 1970b and personal communication, 1977). Forest ecosystems, in particular conifer plantations, might be expected to have high C/P and C/P_o ratios in the soil profile because of a slower phosphorus cycle, high accumulation of organic matter on the soil surface and high C/P ratio in the litter. Although the effects of afforestation on the carbon–phosphorus relationships in whole soil profiles have not yet been studied, the fact that some profiles under plantations of Sitka spruce can have substantially higher ratios (C/P 53-315; C/P_o 105–514) than those under several upland grasslands (C/P 20–66; C/P_o 41.5-107) (Floate 1962) supports this conclusion. It appears, therefore, that the grazing of upland grasslands by sheep may slow down or reverse the natural pedogenetic changes in soil phosphorus forms, leading to soil improvement (Floate 1970b) and conifer forests may promote the trend towards infertility. Deciduous woodlands have intermediate C/P and C/P_o ratios and probably have, therefore, intermediate effects on changes in phosphorus (for Meathop Wood, see Floate 1962).

REMOVAL OF PHOSPHORUS BY CROPPING

Removal of phosphorus in timber and sheep products can potentially reduce the amount of phosphorus cycling in the forest or grassland. From a 50-year-old forest 4–14 kg P ha^{-1} in thinnings and 8–22 kg P ha^{-1} (averaging 0.25–0.7 kg P ha^{-1} yr^{-1}) will be removed in timber (Table 1), if slash and root systems, which contain considerable amounts of phosphorus (Nykvist 1974), are left on site to decompose. Modern trends in forestry, because of pressures to increase wood supply, are to clear-fell and remove all above-ground tree material, to harvest whole trees including stumps (Keays 1974) and possibly to reduce rotation times to 30 yr. By clear-felling and whole-tree harvesting on a 50-yr rotation, the amounts of phosphorus removed could almost double (Table 1). Reduction of rotation time from 50–55 yr to 30 yr coupled with whole-tree harvesting could quadruple the amount of phosphorus removed, as trees contain almost as much phosphorus at 30 yr as at 55 yr (Ovington 1959).

The amount of phosphorus removed from upland grasslands in sheep products is 0.1–1.2 kg P ha^{-1} yr^{-1} (Crisp 1966; Newbould & Floate 1978;

TABLE 1

Quantities of phosphorus removed in timber

Harvesting regime	Total P removed $(kg\ ha^{-1}[50\ yr]^{-1})$	References
Thinnings	4–14	Ovington (1959); Rennie (1955)
Trunks only	8–22	Ovington (1962); Weetman & Webber (1972); Nykvist (1974)
Clear-fell (all above-ground production	21–52	Ovington (1962); Weetman & Webber (1972); Nykvist (1974)
Stump removal (assuming 40% extraction)	4–8	Ovington (1962)
Thinnings and trunks only	12–36	
Clear-fell or whole-tree harvest	25–76	

Perkins 1978). The higher rates of removal, more than 15 kg P ha^{-1} (50 yr)$^{-1}$, are usually from relatively fertile zones or from improved pasture, constituting only a small percentage of the upland area in use (Newbould 1975). Thus hill sheep farming currently removes less phosphorus from sites than forestry. If there were a shortening of the rotation time towards a 30-yr forest cycle, forestry would have an even greater impact.

Although these amounts are small by comparison with the amounts removed in agricultural crops (300–1290 kg P ha^{-1}; Russell 1973), they are biologically significant, because the phosphorus is usually removed from poor soils and from the small proportion of the total phosphorus in the ecosystem which is cycling. It is often assumed that the amounts of phosphorus removed from forests by thinning and conventional logging or from upland grasslands by low-intensity grazing can be met by natural inputs from rainfall and rock weathering. Although this might be a valid assumption in some areas where rocks weather fairly rapidly, it is not generally applicable because with some soils leaching losses may exceed input in rainfall (Viro 1953) and, particularly in forests, amounts equivalent to inputs may be consumed in the accumulation of organic matter. Thus removal of phosphorus, however little, may have a long-term effect on soil fertility.

Clearly fertilizers can be used to great advantage in forests and upland grasslands, as they can release plant production, at least temporarily, from its dependence on natural cycling processes and replace the phosphorus removed by cropping. Although the use of fertilizers is increasing (Binns 1975;

Newbould 1975), a large area of the uplands is still irregularly fertilized or remains unfertilized. Whether or not fertilizer is applied, the aim of land management should be to stimulate the natural phosphorus cycle and to reduce the removal of phosphorus in crops. To do this, more needs to be known about the quantitative relationships between the processes and quantities in the phosphorus cycle and how they are affected by the cycling of other nutrients and by environmental and management factors. Because of the complexity and the interactive and dynamic nature of these processes, complicated mathematical models of the kind outlined by Katznelson (1977) or those developed for studying the behaviour of nitrogen in soils by Beek & Frissel (1973) will be necessary. Such studies then could lead to a more substantial long-term improvement of the poor, phosphorus-deficient upland soils (as visualized by Crompton 1958) than can be brought about by fertilizers alone.

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Discussion

Arthur: How large are the experimental areas?

Harrison: Both experimental areas were about 1 ha. However, each experimental area was surrounded by about 30–40 ha with similar vegetation.

Arthur: How did you sample these heterogeneous systems to determine these phosphorus levels?

Harrison: The methods will be described at length in publications which are in preparation at present. Suffice it to say, we have replicated the figures as much as possible to reduce the errors for the values for each component in Figs. 1 and 2. Our figures for the woodland area compare favourably with those (Table 1) for a similar oak, ash and hazel woodland in Belgium (Duvigneaud & Denaeyer-de Smet 1970).

Nielen: The difference in figures for the input from rain (Figs. 1 and 2) may

TABLE 1 (Harrison)

Comparison of aspects of the phosphorus cycle for Meathop wood and a comparable Belgian woodland

Compartment or transfer	Meathop Wood	Virelles (Belgium)
Annual uptake by trees and shrubs	8.8 kg ha^{-1} yr^{-1}	9.4 kg ha^{-1} yr^{-1}
Annual uptake by ground flora	2.6 kg ha^{-1} yr^{-1}	2.0 kg ha^{-1} yr^{-1}
Annual P retention in tree production	1.4 kg ha^{-1} yr^{-1}	2.0 kg ha^{-1} yr^{-1}
Total P content of soil	1800 kg ha^{-1}	2200 kg ha^{-1}

be explained not only by the differences in average rainfall but also by the fact that the phosphorus content of the rain comes from erosion and is brought into the atmosphere by wind. Over certain areas (especially woodlands) the amount of phosphorus eroded will be lower than over flat agricultural regions.

Pirie: How much of the 40 kg P ha^{-1} in the conifer litter (p. 183) comes down each year?

Harrison: Although the amount varies with the different productivity of forest ecosystems, it is usually in the same order as that in deciduous woodland, from 1.2 to 10 kg P ha^{-1} yr^{-1}.

Pirie: Is the figure for the standing dead mass uniform for almost all species? I am interested in the calcium/phosphate ratio and the extent to which a calcium-rich leaf would hold phosphate back, because in most work on tobacco, beans and similar species used for virus work, addition of phosphate to a leaf extract almost always precipitates the calcium which is present in excess. Would, for instance, a nettle, which is calcium rich, hold back more phosphate in the leaf when it dies?

Harrison: I don't know; I have not investigated that. Different species may have different concentrations within the plant material. For example, *Nardus* grass may have 0.10–0.14% P (or less in senescent tissue), whereas *Agrostis* and *Festuca* grass may contain more phosphorus. The higher the concentration of phosphorus or nitrogen in plant litters the faster they decompose on the soil surface. This probably has repercussions on soil development.

Pirie: I also wonder to what extent calcium and phosphate are compartmented, because when leaf is extracted, normally at pH 5.7–6.0, calcium phosphate ought to precipitate, but it does not.

Tinker: Your figure of 0.1–0.14% P is high for tissue in upland grassland.

Harrison: The ecosystem we studied overlies pumice tuff, which is rich in phosphorus. The poorer the phosphorus content of parent material, the lower the phosphorus content of the ecosystem and hence, broadly speaking, its fertility. Rocks like slate and shale, for instance, are poorer in phosphorus and do not weather as quickly as pumice tuffs and, therefore, the replenishment of phosphorus cycling in the system from the weathering of rocks will vary with different systems. This may partly explain the phosphate deficiency in the UK uplands where parent materials are usually poor in phosphorus and do not weather rapidly.

Larsen: You estimate two different figures for the 'available' phosphorus in each ecosystem (see Figs. 1 and 2). How do you define 'available'?

Harrison: For both systems we used somewhat arbitrary methods. For the upland grassland so-called available phosphorus was measured by leaching soil columns with water until phosphorus release stopped. The figure

obtained indicates that the amount of phosphorus the water can get at is somewhat low.

The soil in Meathop Wood is highly deficient in phosphate, as indicated by several points. Both Barabara Mosse (Rothamsted) and I have had difficulty in growing plants on soils taken from the wood but additions of phosphate fertilizer to pots can increase plant growth up to 700%. Also, using Piper's method (Piper 1950) for measuring phosphorus sorption capacity of Meathop soil, we obtained figures in the order of mg P/(g soil). As the total phosphorus content of soil is around 600 µg/(g soil), the sorption capacity is far greater than the total P content. The value of about 3 kg P ha^{-1} for 'available' phosphorus was obtained by two methods: (i) extraction of phosphorus by 2mM-H_2SO_4 (1:125 w/v) and (ii) a physiologically based assay we have developed from Bowen's rapid test for phosphate deficiency in plants (Bowen 1970). We have demonstrated the value of the method in determining the available P in poor soils, for which chemical methods tend to be unreliable.

Larsen: I must say that I think your figures for available P are meaningless! They may be out by as much as several orders of magnitude. I recommend that you use more up-to-date methods, for instance extraction with sodium hydrogen carbonate ($NaHCO_3$) as anion-exchange resin. By use of various witches' brews, you cannot decide whether the phosphate level is high or low.

Harrison: I tried to measure the L value but failed. Plants grown in soil to which we added [^{32}P]orthophosphate, about 15 µCi/(kg soil), had not much greater than background levels of radioactivity in them.

Larsen: The L value method probable did not work because the soil is highly deficient.

R. J. P. Williams: What is the L value?

Larsen: It is the quantity of soil phosphate exchanging with added $^{32}PO_4$ in pot experimental conditions (Larsen 1952). Use of an anion-exchange resin would, however, be more practical. About two thirds of the isotopically exchangeable soil P can be removed by resin. [cf. p. 132.]

Harrison: That is a useful suggestion. However, the phosphate in Meathop Wood soil is very to be inaccessible to plants.

Larsen: Did you use a carrier for $^{32}PO_4$?

Harrison: No—in case I disturbed the phosphate equilibria in the soil.

de Oude: The problem of availability of phosphorus is also important for lake systems. A 0.01 mol/l solution of nitrilotriacetic acid is used (Golterman 1973) to estimate the amount of phosphorus that sediments can make available to the water body. This problem needs to be solved if we are to judge the feasibility for restoring hypertrophic lakes and to estimate the time it will take for the lake to recover.

Tinker: I must congratulate you, Dr Harrison, on the completeness of these balances. However, my comment is that in the whole system some of the pools contain several hundred kg P ha^{-1}. The transfers within the system are of the order of tens of kg P ha^{-1} and the inputs and outputs of the system are an order smaller. Such a range of values raises doubts about the relative accuracies; slight errors in the large pools will produce massive errors in the smaller values dependent on them.

My question arises because some time ago I did nutrient-cycling work, and eventually wondered what to do with all the data I had obtained. The salient figures here seem to be the amounts held in the litter layer, and that should be relatively easy to measure and may have practical value. Is it then worth collecting the other data (i.e. for fungi, bacteria and so on)?

Harrison: We set up the programme to examine the distribution and circulation of major nutrients including phosphorus within the two eco-systems. The exercises have been useful in that they have indicated many important aspects of the cycles, among them the role of the litter layer in the balances within the ecosystems. Removal of the litter layer from forests can decrease the productivity of trees in successive years and continued removal can decrease the site quality for forestry. One could perhaps argue that removal of litter takes away nutrients other than phosphorus, such as nitrogen, but significant amounts of nitrogen come into forest ecosystems in the rain, and nitrogen can be fixed on the surfaces of tree leaves, so it appears that the effect of litter removal is not explicable in terms of loss of nitrogen. As potassium is usually not limiting I conclude that the effect is caused by a phosphorus deficit.

Tinker: That is what would happen in any cropping system when the crop is removed.

Kirby: The large figure for the store of organic phosphate in the woodland soil (Fig. 1) surprised me. The inputs suggest that the turnover of organic phosphate takes about a couple of hundred years. Is that right?

Larsen: Yes.

Harrison: From carbon-dating work on the soil organic matter it appears that the turnover rate of carbon is in the order of hundreds of years, although some surface carbon turns over rapidly (i.e. it contains bomb carbon-14). On the assumption that the turnover of carbon reflects that of phosphorus bound in the organic form, then much of the organic phosphorus is practically immobile.

Kirby: I'm pleased with that conclusion. When I measure the rates of hydrolysis of phosphate esters, I frequently say that, in neutral conditions, diesters and monoesters will have half-lives of hundreds of years or so, but of

course I don't have actual measurements to support that statement!

R. J. P. Williams: Dr Harrison, are you interested in getting that organic phosphate to turn over as fast as possible?

Harrison: Not too fast. If the organically bound phosphorus were to turn over too fast, we could be faced with considerable leaching losses from soils, which could generate eutrophication problems in bodies of water as well as depleting the quantity of phosphorus held in the soil profile. It would, however, be useful if we could optimize turnover in relation to plant demand for phosphorus.

R. J. P. Williams: But yields are phosphate-limited while ample supplies of phosphate are stored as organic matter which has gone through the cycle and is stuck in soil for hundreds of years. One way to increase yields is to add fertilizer even though some of that becomes locked up as organic matter.

Harrison: Though some phosphorus originating from fertilizer may get fixed in the organic form in soils, much gets fixed in the inorganic form by iron and aluminium.

R. J. P. Williams: So that is lost as well. The alternative is to mobilize the organic pool. What is a reasonable optimal time scale for turnover which would assist all these lands?

Harrison: One cannot give an universally applicable time scale for optimum turnover of the organically bound phosphorus: so much depends on soil characteristics, the vegetation types and its phosphorus demand. However, only small increases in mineralization of organic phosphorus can make significant changes in the phosphorus 'available' to the plant.

Kirby: That could be done by slightly lowering the pH from pH 5.

Harrison: No.

Larsen: Liming increases the rate of mineralization.

Kirby: That is to be expected for high-pH soil, but is it true also for a low-pH soil?

Larsen: Liming will help in any situation where phosphate is locked up in organic form.

Harrison: Limed fields are immediately obvious in the uplands by their greenness.

R. J. P. Williams: Is the chemistry of increasing the pH and free phosphorus concentration by liming totally clear?

Larsen: Yes.

R. J. P. Williams: So improvements in microbiology seem to be more important than improvements in the chemistry.

Loughman: There is a case for selecting strains in which phosphatase activity is higher for reseeding in those conditions.

Harrison: That may help. The root systems of plants which are deficient in phosphorus produce higher amounts of phosphatase enzymes, so possibly helping to mobilize organic phosphorus. But solubility of the organic phosphorus in the soil is also a problem; I wonder whether enzymes can help to solubilize insoluble substrates.

R. J. P. Williams: In summary, a major problem seems to be that a lot of the phosphorus is locked up in organic materials; phosphate is not really scarce but inaccessible and, at present, we do not know how to speed up the cycling of that phosphorus.

Harrison: In forests of conifers, one possible way to do that is to interplant the conifers with broad-leaf species, in particular birch. The leaf litter from birch trees accelerates the decomposition of pine and spruce litter which in turn speeds up the release of nutrients leading to increased tree productivity. Blintsov (1971) and Kavalev (1969) have demonstrated up to 20% increases in spruce productivity by interplanting with birch.

Emsley: Two years ago the Australians tried to prevent forest fires by burning off the top litter every year. I wonder whether, as a result, the yields from their forests had increased.

Harrison: It may have done. But in the UK, the Forestry Commission's fear of fire is likely to discourage its use for this purpose.

Shaw: It has been suggested, especially in Australia, that the heat generated by such brush fires, which spread quickly, is insufficient to start major forest fires.

Harrison: In Sweden, burning of the organic debris on the soil after clear-felling releases only a small amount of the phosphorus bound in it (Nykvist 1974).

Emsley: Repetition of the process yearly or every other year should release it.

Harrison: After the trees have been felled the cleared area is often rapidly replanted. So that method may be inapplicable.

Emsley: In clear-felled areas such burning could speed up the run-off of phosphate.

Bowman: The removal of phosphorus from forested areas may increase considerably in future. At present about 30–40% of the tree is harvested and the rest is left to decay, but newer harvesting techniques aim to take almost all the tree, roots and all.

I suspect that Europe will have to afforest a great deal more than it has at present. This substitution of trees for rough grazing land (of which the UK and Europe have large areas) may increase the loss of phosphorus. We should concentrate on finding species of trees, as well as plants, that can cope with low soil concentrations of phosphorus.

Harrison: Lodge-pole pine can be planted and will grow successfully in areas where sitka spruce will not unless fertilized. Species of tree seem to be available, but unfortunately the market for the wood is not so good as for sitka spruce, so there is a reluctance to change. Also, if increasingly more phosphorus is extracted from poor soils by trees which have a higher capacity for extraction of phosphorus, soils will be depleted by phosphorus to an even greater extent.

McClellan: Nothing prevents you from fertilizing trees!

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Phosphorus and the eutrophication of lakes—a personal view

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Abstract The availability and abundance of biologically-active forms of phosphorus in natural waters are briefly reviewed in relation to the requirements, growth and development of algal populations. The consequences of artificial enrichment of lakes with agricultural, domestic and industrial effluents ('eutrophication') attributed to increased phosphorus loading are compared with evidence from a selection of natural lakes and experimental systems in the UK. The suggestion is made that increased loadings on richer lakes make relatively less impact than does mild eutrophication of unproductive waters. Within limits the effects of eutrophication are reversible.

This account is necessarily a personal one. The literature published on various aspects of eutrophication—the artificial enrichment of lakes and impoundments by biologically-active substances from agricultural, domestic and industrial sources—is so large, and much of it is either apparently or actually contradictory, that it is impossible to review it objectively in a short communication. Instead, I have attempted to illustrate the main aspects of the problem and especially those arising from the additional production of planktonic algae, largely by reference to experience and data obtained from British waters in the course of the research done at the Freshwater Biological Association. A broader insight into the same problems, and with particular reference to those involving phosphorus, may be gleaned from Rohlich (1969), Lund (e.g. 1972) and Porter (1975).

AVAILABILITY OF PHOSPHORUS IN NATURAL WATERS

Phosphorus is one of 20 or so elements known to be essential to the growth of all plants, including the algae. It is a component of nucleic acids and of adenosine triphosphate, the basis of enzyme synthesis and energy transfer

systems at the cellular level. But phosphorus is not often freely available in natural waters and, together with nitrogen, it is one of the elements whose availability provides a major constraint on the production of large crops of planktonic algae. Phosphorus is often (though not always) the limiting element in aquatic ecosystems (Lund 1965; Schindler 1977).

Phosphorus usually occurs in the oxidized state, either as ions of inorganic orthophosphate (HPO_4^{2-}, $H_2PO_4^-$) or in organic, mainly biogenic, compounds. Phosphates in lakes are derived from the weathering of phosphatic minerals in their catchment areas and from the leaching of catchment soils and terrestrial ecosystems. The concentrations of biologically active phosphates in UK lakes generally vary within the range 0.1–1000 μg P l^{-1}. Measurement is complicated by seasonal variations in supply and biological uptake and by chemical and biological transformations. The principal pathways (shown in Fig. 1) have been traced and equilibrium constants have been evaluated (see Stumm & Morgan 1970; Lean 1973; Rigler 1973). Moreover, the biological cycling of phosphorus can be extremely rapid (Rigler 1956); sedimentation of algae and the faecal pellets of grazing animals together with microbiological uptake combine to accelerate the flux of phosphorus to the sediments (see e.g. Jackson & Schindler 1975). The sediments thus provide a major reservoir of phosphorus. Events near the lake bottom, especially where this is overlain by an anoxic hypolimnion, lead to further complexing and exchanges of phosphorus by iron, aluminium and organic substances. The rate of release of phosphate, which may be available to algae (Golterman et al. 1969), varies widely (0.8–18 mg P m^{-2} d^{-1}; see Serruya et al. 1974; Lean & Charlton 1976; Sonzogni et al. 1977) and may
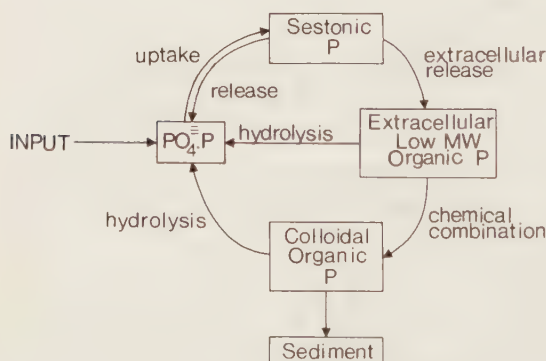
FIG. 1. Principal phosphorus pathways in freshwaters (based on Lean 1973).

exceed the flux to sediment. The prevailing steady-state depends on a multiplicity of factors, including sediment composition, pH, redox potential, temperature, morphometry and water movements, as well as the rate of input of phosphorus and the level of biological production within the water itself.

These various factors render it difficult to establish, at least on any routine basis, the fraction of total phosphorus that is available for supporting plant growth. For most practical purposes, then, the investigator must normally make do with a series of spot determinations of total and reactive phosphorus, the rate of input of phosphate (the specific loading rate) into the system and, at best, a superficial knowledge of the magnitude of the fluxes and losses of phosphorus. These quantities will be peculiar to any individual water body. In spite of the publication of several elegant models of case studies, the experiences gained in one lake cannot necessarily be applied to predict the consequences of phosphorus enrichment in another.

Considering the complexities of the phosphorus system in lakes, it is difficult to characterize the chemical effects of artificially increased phosphate loadings which become largely integrated into the existing transformations. Nevertheless, the significant advances in agricultural productivity facilitated by inorganic fertilizers, the growth of industrial output, and the improvements in living standards brought about by mains water supply and drainage installation have together led to an average increase in the amount of phosphate reaching water supplies. Modern detergents, which may contain up to 30% by weight of polyphosphate, have been especially implicated in instances of lake eutrophication: polyphosphates are rapidly hydrolysed in microbial processes in sewage treatment plants and in lakes (see e.g. Clesceri & Lee 1965).

Where long-term records of the chemical composition of lake waters have been maintained, average increases in the concentration of dissolved reactive phosphorus have often been observed to correspond with trends in enrichment. In Fig. 2 the mean winter (i.e. 1 December–31 January period) concentrations of phosphate phosphorus in three of the lakes studied by the Freshwater Biological Association are compared with examples of annual agricultural sales and detergent production. Although based on fewer data collected over a shorter period, a significant response in Crose Mere is apparently lacking. The catchment of this small, naturally eutrophic, lake is intensively agricultural but sparsely populated, and the lake receives no direct sewage effluent (Reynolds 1973a). Windermere and Blelham Tarn, however, receive substantial amounts of treated sewage (see Lund 1972, 1978 for further details).
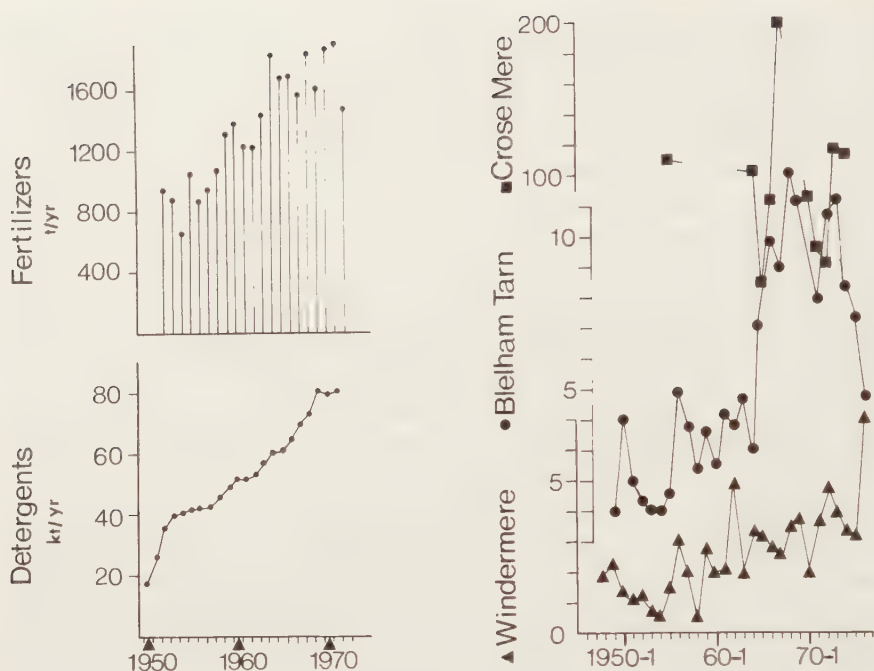
FIG. 2. (Left, above) Annual supplies of phosphatic fertilizers to farms in the former county of Westmorland, UK; (below) annual sales of detergent in the UK, in kt (redrawn from data of Lund 1978); (right) mean concentrations of dissolved reactive phosphorus in the period 1 December–31 January, in successive winters in the north basin of Windermere (▲), Blelham Tarn (●) and Crose Mere (■).

PHOSPHORUS REQUIREMENTS OF PHYTOPLANKTON POPULATIONS

The forms of phosphate which are available to most algae are broadly the same unpolymerized forms detected by the standard acid–ammonium molybdate reduction method used for orthophosphate determinations (Lund 1965; Reynolds 1971), and they can be taken up from very low external concentrations ($< 1 \, \mu g \, P \, l^{-1}$). Uptake is endothermic (energy requiring) and is most rapid in phosphorus-starved cells, but the element can be absorbed and stored in excess of immediate requirements ('luxury consumption'). Mackereth (1953) established that the absolute minimum phosphorus content of the diatom *Asterionella formosa* Hass. is about $0.06 \, \mu g \, P \, 10^{-6}$ cells (i.e. about 0.02% of its dry weight, and about 0.04% of its ash-free dry weight). Below this limit the cells are unable to grow and divide. Cells exposed to phosphorus-enriched media, however, contained up to $0.4 \, \mu g \, P \, 10^{-6}$ cells,

enough theoretically to support three cell divisions in a phosphorus-free medium! The percentage phosphorus contents of various planktonic algae have since been shown to be of a similar order, in the range 0.03–0.8% of ash free dry weight (Rodhe 1948; Round 1965; Lund 1965, 1970). Except at low population densities, the external concentration of dissolved reactive phosphorus present provides no reliable measure of the phosphorus available; nor does it allow more than a rough prediction of the likely population maximum to be made. Moreover, natural populations rarely increase to the absolute limiting cell concentration, because the rate of growth is significantly reduced before that point is reached. Specific growth rates have been determined for several algal species in batch- or continuous cultures (see e.g. Owens & Esaias 1976) and these characteristically vary with the concentration of nutrient available, in accordance with the Monod equation (1), where μ is

$$\mu = \mu_{max} S/(K + S) \tag{1}$$

the growth rate, μ_{max} is the maximum growth rate, S is the amount of nutrient available and K is the 'half saturation content' (whose derivation is represented in Fig. 3), the cell substrate concentration which will sustain a growth rate of $0.5\mu_{max}$. The term K provides a useful expression of the growth potential of a species but both K and μ_{max} vary interspecifically. Since growth in natural conditions is influenced by a multiplicity of environmental factors, laboratory findings cannot be extrapolated directly to natural populations. For many purposes, it is appropriate to adopt Gibson's (1971) view of limitation, that is that a given factor is not limiting if an increase in that factor produces no significant stimulation of algal growth. In this way, the laboratory bioassay technique, which measures the potential algal growth in filtered lake water spiked with selected nutrient combinations (Skulberg 1964; see also Maloney *et al.* 1973) provides a useful tool in identifying limiting nutrients and predicting the response of algal production to enrichment.

THE BIOLOGICAL CONSEQUENCES OF PHOSPHORUS ENRICHMENT

Quantitative effects

If biological production in an aquatic ecosystem is limited by phosphorus, a consistent increase in the phosphorus loading rate, from whatever source, is likely to lead to increased production of phytoplankton and, usually, larger standing crops. The results of a recent enrichment experiment which we did in the experimental enclosures (Lund Tubes) installed in Blelham Tarn, Cumbria, illustrate this point particularly well. (The design and operation of
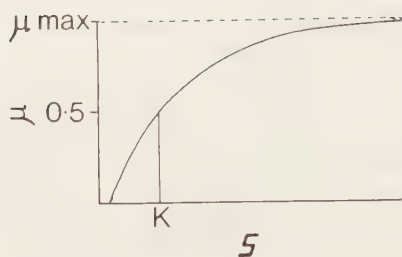
FIG. 3. The relationship of growth rate (μ) to nutrient concentration (S); K is the concentration which will support a growth rate of $0.5\mu_{max}$.

these enclosures is fully described in Lack & Lund 1974.) Before closure of the two tubes in Spring 1977, the reactive phosphate concentration of the Tarn water ($< 0.6 \mu g \, P \, l^{-1}$) was unusually low, after high autumnal flushing and an early winter growth of cryptomonad flagellates. By March, the dominant alga was the diatom *Melosira italica* (Ehr.) Kütz. subsp. *subarctica* O. Müll but its slow growth was symptomatic of phosphorus limitation: the cellular phosphorus content of the alga was 0.023% dry weight, that is, close to the absolute minimum. Bioassay of the lakewater, using *Asterionella* as the test organism, confirmed the phosphorus-limiting condition (Fig. 4A). Tarn water was isolated in each tube on 23 March; tube B was immediately fertilized with a potassium hydrogen phosphate (KH_2PO_4) solution to raise the available phosphorus concentration to 20 $\mu g \, l^{-1}$ and at weekly intervals thereafter to restore the concentration to 20 $\mu g \, l^{-1}$ on each occasion; tube A was left unfertilized. Bioassay of tube B water, sampled on 6 April, indicated that phosphorus was no longer a limiting factor (Fig. 4B). The response of the algal population in tube B to the fertilization was rapidly to increase in biomass, represented in Fig. 5 by chlorophyll *a* concentration, as predicted by the assay. But the specific growth response of *Melosira* was relatively less than that of *Asterionella formosa*, *Cyclotella* and *Stephnodiscus* spp., which eventually became dominant. The mean rate of increase of the *Asterionella* over the three weeks after fertilization was 0.143 ln units d^{-1} (equivalent to a doubling time of 4.8 d); this may be compared with maximum rates of vernal populations observed in other lakes at similar temperatures (see Lund 1950; Reynolds 1973*b*), and with the contemporary rate of increase of *Asterionella* in tube A (0.099 ln units d^{-1}; doubling time 6.9 d). This apparently clear-cut result supports the contention that phosphorus enrichment of standing waters inevitably leads to the larger algal crops that may detract from the visual appearance of lakes and increase treatment costs of water supplies held in storage reservoirs. However, it also demonstrates that the relationship be-
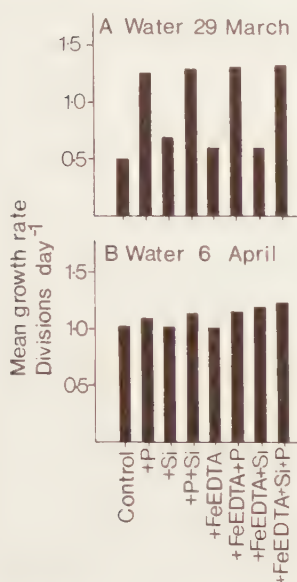
FIG. 4. Growth responses of *Asterionella formosa* in bio-assays of the waters indicated, and in water enriched with the nutrients and in the combinations shown. (For procedure and concentrations see Lund *et al.* 1975). EDTA, ethylenediamine tetraacetic acid.

tween increased phosphate loading and increased algal productivity is not a simple one. The phosphorus consumed in tube B between 23 March and 26 April (23.8 μg P l^{-1}) was not matched by additional algal chlorophyll (chl a) production in the prefertilization ratio (2.61 μg chl a [μg P]$^{-1}$). Had this been the case, an algal population equivalent to 76 mg chl a l^{-1} might have been predicted.

One possible contributing factor is the disturbance to the phosphorus equilibrium brought about by altering the concentration of one of its components. The increased ionic phosphate concentration also allows an increased cellular phosphorus content to be maintained. another aspect of the result which requires explanation is the apparent limitation of the phyto-plankton growth at about 25–27 μg chl a l^{-1}. This is almost certainly due to the intervention of other factors; as one limiting condition is alleviated, growth may proceed until it, or another factor (e.g. nitrogen), imposes a new constraint upon the alga. In the case in question, this was probably not chemical, but physical, namely, the reduction of average photic conditions to which the population in the mixed, optically deep, water column of the Blelham tube is exposed (cf. Talling 1971).
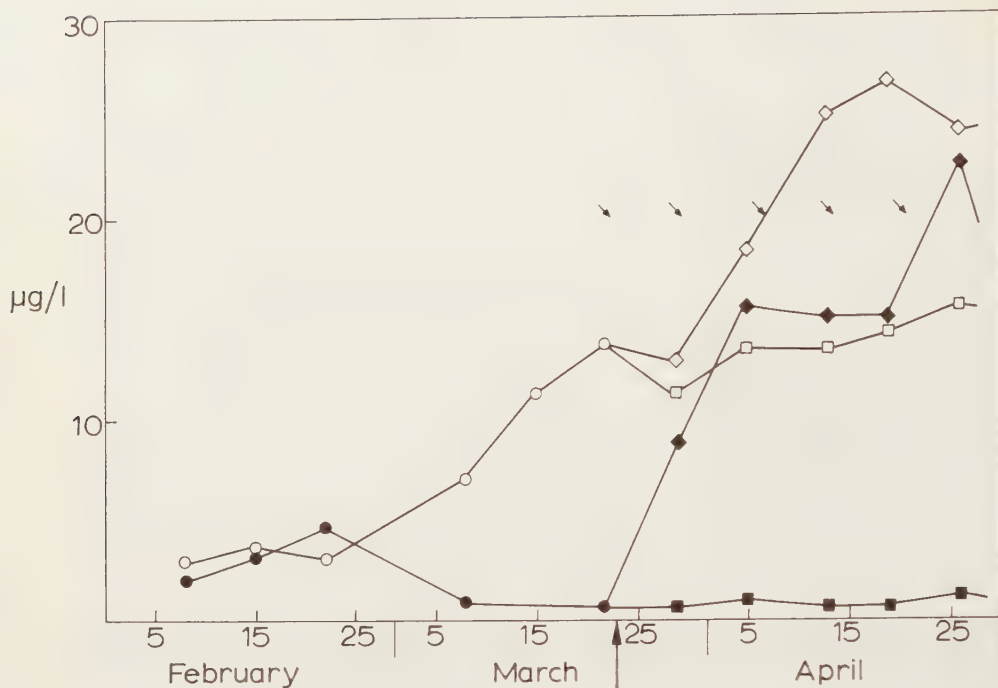
Fig. 5. Dissolved reactive phosphorus (solid symbols) and chlorophyll *a* concentrations (open symbols) in Blelham Tarn (circles) and in the tubes A (squares) and B (diamonds) after closure from the lake (indicated by vertical arrow). The small oblique arrows indicate the dates when phosphorus was added to tube B to restore the concentration of dissolved reactive phosphorus to 20 μg l^{-1}.

Experience gained in the long-term study of lakes is substantially supported by the experimental results. In Fig. 6 the recorded maximum sizes of recent vernal algal maxima in Windermere (North basin), Blelham Tarn and Crose Mere are represented by their chlorophyll *a* content (uncorrected for phaeopigment). Though there is evidently a general trend for the first two basins to have produced larger crops over the past decade or so, there is no significant correlation between the chlorophyll maximum and the preceding mid-winter phosphate concentrations in any of the three lakes (see Fig. 2: correlation coefficients -0.13, -0.14 and $+0.14$, respectively). When all the points are treated simultaneously, a highly significant correlation ($r = +0.88$, $n = 34$) is detected (Fig. 7). In this respect, the data support the findings of workers elsewhere (e.g. Dillon & Rigler 1974, 1975; Vollenweider 1975; and cf. Schindler 1977) that there is a close relationship between total phosphorus content and average algal standing crops in a wide variety of lakes. However,
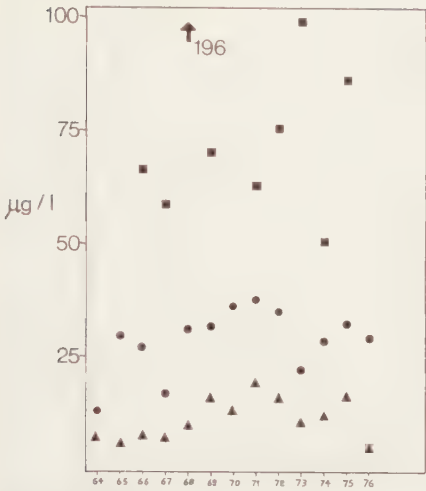
FIG. 6. Vernal chlorophyll maxima in (▲) Windermere (North Basin), (●) Blelham Tarn and (■) Crose Mere since 1964.
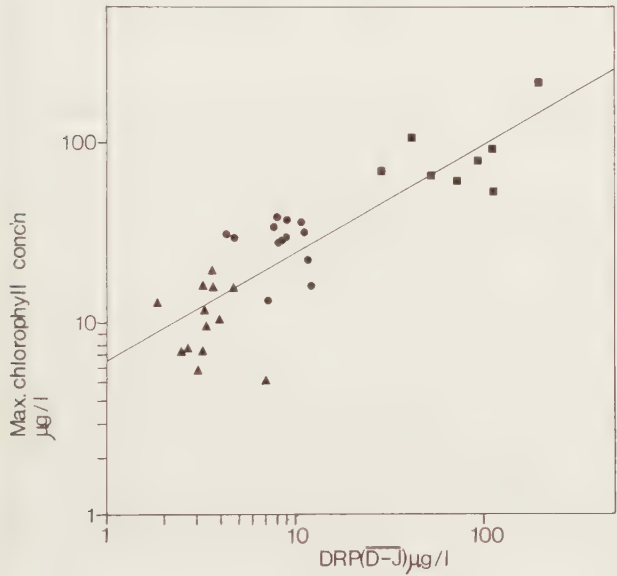
FIG. 7. The relationship between vernal chlorophyll maxima and the mean concentration of dissolved reactive phosphorus (DRP) the previous winter (see Fig. 2) in (▲) Windermere (North basin), (●) Blelham Tarn and (■) Crose Mere.

TABLE 1

Phosphorus use in three lakes

	Windermere North Basin	Blelham Tarn	Crose Mere
Mean winter phosphate[a] (μg P l^{-1})	3.52	8.52	89.8
Predicted mean maximum chlorophyll concentrations[b] (μg l^{-1})	13.1	22.4	87.7
Chlorophyll production/phosphorus available	3.72	2.63	0.98

[a] From Fig. 2.
[b] From Fig. 7.

it must also be pointed out that the vernal use of available phosphorus is apparently more efficient in dilute lakes, as can be judged from Table 1. Indeed, the size of the vernal maximum in Crose Mere appears to be rarely subject to nutrient limitation, but is more likely governed by light availability in the mixed water column (Reynolds 1973b). If data on the optical properties of Crose Mere and on the photosynthetic behaviour of vernal phytoplankton populations in this lake are interpolated into Steel's (1972) model of the light relationships of diatom maxima in mixed reservoirs (see Appendix A for solution of the model), the size of the population (in terms of chlorophyll concentration) at which light begins to limit production may be predicted to be greater than 107 μg chl a l^{-1}. Thus, it is proposed that Crose Mere already supports maximal vernal algal crops when it is fully mixed, which further phosphorus loading could scarcely increase. Moreover, a hypothetical reduction in phosphate loading on the lake, to give a concentration of only 40 μg P l^{-1} in midwinter, might not significantly reduce the size of the vernal maximum if the efficiency of its use of phosphorus was to improve to (say) the Windermere level. For the same reasons, it follows that a modest increase in phosphorus loading on a phosphorus-deficient lake is likely to lead to a larger rise in the level of algal productivity and biomass that can be supported, and hence in its detraction from water quality and appearance, than a proportionately similar increase on a lake in which phosphorus is more freely and continuously available.

Qualitative effects

A sustained input of nutrients into a lake may, subject to other factors,

contribute to the maintenance of larger algal crops throughout the summer period, though these are rarely the same species which participate in vernal maxima. Generally, the diversity of species present in the plankton is greater in stratified conditions than during winter–spring mixing (Margalef 1968; Reynolds 1976). In more eutrophic lakes, green algae, blue-green algae, dinoflagellates and euglenoids often feature in the seasonal succession, and the initial appearance of large populations of *Aphanizomenon*, *Anabaena* and *Microcystis*, or increased populations of *Ceratium*, *Sphaerocystis* and *Eudorina* have been observed in hitherto phosphorus-deficient waters of the English Lake District over recent years (Lund 1973, 1978). The mechanisms 'triggering' these invasions are still largely unknown, particularly as the nutrient requirements of individual species are, weight for weight, generally similar, but it is possible that the 'invading' species have faster intrinsic rates of growth which are of competitive advantage when nutrients are more freely available. Equally, they may be stimulated by other interactions with chemical and physical modifications to the enriched lake system.

In particular, the advent of bloom-forming blue-green algal populations, allegedly as a direct consequence of lake eutrophication in developed countries, is regarded as being especially objectionable, owing principally to their tendency to form buoyant surface scums; although the blue-green algal biomass may be actually relatively small, blooms give an exaggerated view of their abundance (Reynolds & Walsby 1975). It is the blue-green algae, perhaps more than any other algal group, which most arouse public concern over eutrophication of lakes, especially when recreational or sporting waters are affected. In spite of reports of toxic blooms (e.g. Gorham 1964) and local deoxygenation after the collapse of the blooms (Barica 1975), their mass appearance in a lake need not be regarded as the penultimate stage in its 'death', as is often popularly supposed.

REVERSAL OF EUTROPHICATION

Although I take the view that the so-called 'problem' of eutrophication is often overstated, it is not to say that it should be regarded as harmless or acceptable, or that, in some cases, attempts should not be made to avert the worst consequences of lake enrichment. Schemes to direct sewage from lakes, to remove phosphates in sewage by precipitation with iron(III) chloride (see Thomas & Rai 1970), or to reduce the load of detergent polyphosphates in water, though feasible technically, are extremely expensive alternatives. Moreover, it would be difficult to find a suitable replacement for phosphate in detergents with similar non-toxic properties (cf. Lund 1972). In many in-

stances, it would be cheaper to devise physical growth limitation, for instance, through artificial mixing (see Ridley 1970; Steel 1972). In the UK, where lake eutrophication is not a serious problem, principally because effluents from populous centres are discharged into rivers, rather than lakes, lake restoration schemes have been scarcely considered, but Lough Neagh (our largest inland water) is an obvious exception. The problems are experienced more acutely in the USA and in some European countries where major cities discharge, or have discharged, their effluents into nearby lakes, and attempts to reverse eutrophication have been justified largely on the grounds of damage to amenity and recreation (Edmondson 1970). The spectacular recovery of Lake Washington since 1964, when the progressive diversion of all major sewage sources entering the lakes was commenced (see e.g. Edmondson 1972), confirms that much can be rapidly achieved if the eutrophication is still relatively mild (cf. Lorenzen 1974). The Blelham enclosures (see above) have also been observed to revert to supporting a low algal biomass shortly after phosphorus is excluded (Lund 1975). These instances demonstrate clearly that eutrophication is not a natural successional process; indeed, chemical and fossil evidence from lake sediments (e.g. Pennington *et al.* 1972; Tallis 1973) indicates that the biota and productivity of lakes have fluctuated in response to natural climatically-induced variations in nutrient loading. In more enriched lakes, however, public opinion may demand rapid results; reduction in the external load of phosphorus upon the highly eutrophic Lake Trummen in Sweden did not bring the desired improvement in water quality, until the upper layers of the phosphorus-rich (and other nutrient-rich) sediment were removed (Björk 1972).

CONCLUDING REMARKS

In spite of a great deal of research, there is no simple solution to the eutrophication problem. This is partly compounded by differing popular and political attitudes. Attractive though 'lake restoration' schemes may appear, they will not be equally successful everywhere. Further investigation might usefully be concentrated on the life-cycle and physiology of 'nuisance' species, with a view to their eventual elimination, in favour of more tolerable algal growths. Alternatively, more research could be directed towards the study of eutrophic lake systems, and to harvesting their biomass for practical use (see, for instance, Bogdanova *et al.* 1975). The moral issues, for instance, whether it is right that costly phosphates should be liberally discarded into the environment by developed societies in preference to improving agricultural production in less developed nations, or whether by financing schemes to reduce

phosphorus loadings in lakes and reservoirs society should be expected to maintain the profits of the chemical industry, have yet to be seriously questioned.

ACKNOWLEDGEMENTS

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APPENDIX A

Application of Steel's (1972) model to estimate the maximum standing crop of phytoplankton in a mixed water body.

The model defines $\bar{n}_{max}$ by equation (1) where $\bar{n}_{max}$ is the maximum mean concentration of chlorophyll; ε_{530} is the vertical extinction coefficient of the water to light of wavelength 530 nm; b_{530} is the increment in vertical extinction per unit of chlorophyll; P_{opt} is the photosynthetic rate per unit population per unit time at the light optimum; Δ is the day length; r is the coefficient of 'relative' respiration ($= R/P_{opt}$, where R is the respiration rate per unit of population per unit time); q is the proportion of lake volume flowing out of the lake; Z_m is the mixed depth; and $f_2(\phi)$ is a light function based on the relationship between the irradiance levels obtaining immediately beneath the lake surface (I'_o) and at the onset of photosynthetic light saturation of photosynthesis (I_k), derived in the development of the original model.

$$\bar{n}_{max} = \frac{1}{b_{530}Z_m} \left\{ \left[\frac{P_{opt} + \Delta f_2(\emptyset)}{rP_{opt}(24+q)} \right] - Z_m \varepsilon_{530} \right\}$$

The approximate values substituted for Crose Mere population are as follows:

ε and b are based on the extinction of light in the spectroscopic block of minimum absorption, that is 0.52 ln units m^{-1} and 0.016 ln units m^{-1} (mg chl a)$^{-1}$ (Reynolds 1978), respectively;

P_{opt} is put at 6.5 mg O$_2$ (mg chl a l)$^{-1}$, the rate measured for *Asterionella*-dominated populations in experiments at 7–8°C (Reynolds 1978 and unpublished results);

$r = 0.062$, the mean ratio of R/P_{opt};

q is not more than 0.002;

$\Delta = 12$, the equinoxial day length when the vernal maximum is achieved;

Z_m is the mean (fully mixed) lake depth (3.6 m);

I_k occurs at not less than 25% I'_o and $f_2(\phi)$ has been evaluated accordingly at about 1.0.

Solution of the model gives $\bar{n}_{max} = 107.5$ mg chl a m^{-3}.

If b is put equal to 0.013, the value derived for *Stephanodiscus* populations in the Crose Mere (Reynolds 1978), but all other values are assumed to be the same, $\bar{n}_{max}$ becomes 132.3 mg chl a m^{-3}.

Discussion

R. J. P. Williams: In contrast to the previous discussion, we are now concerned about the availability of phosphorus being too great, in that organisms grow that are a nuisance (e.g. blue-green algae) or are unexpected and unwanted (e.g. undesirable fish). To some people this is a satisfactory state of affairs, but not to others. The control of the amounts of phosphorus in lake water is now a new problem because the phosphorus comes from man's processes, of one sort or another. (This question will be dealt with again in subsequent papers.)

Nielen: What is the limiting value of P concentration below which there would be no growth?

Reynolds: For algal cells, the limiting concentration of P is 0.04–0.08%.

Gilbert: Although you suggest that light limitation begins at chlorophyll a concentrations of about 100 µg/l, the experiments in Blelham Tarn suggest light limitation at a much lower concentration (Fig. 6).

Reynolds: Yes, this discrepancy is due to the morphometric component. The shape of most lakes resembles a flattish saucer rather than a deep U. As the experimental tube we used sits in deep water its morphometric characteristics model those of a deep lake—it lacks shallow water. If the light

penetrates only half way down the tube, half the mass of water will remain in darkness whereas if the lake were saucer-shaped the same penetration of light would illuminate much more than half the volume of water. Consequently chlorophyll a will limit the penetrance of light at lower concentrations in the deeper lake. Such morphometric considerations must be taken into account before one makes statements about phosphorus limitation or light limitation. The figure of 107 μg chl a l^{-1} for Crose Mere was calculated using published models and it agrees well with the observed value. It follows that, above this concentration of chlorophyll a, the net standing crop is unlikely to increase. Of course, this figure is peculiar to Crose Mere, although it may be similar in other lakes. Steel, whose model I used, showed that the figure for a Thames Valley reservoir might be 116 μg/l. For the ultra-deep 'lake', the figure is around 27 μg/l.

Alexander: You have stressed that all lakes differ and that one cannot generalize conclusions for one lake to any other particular lake, and I agree. What are these different lakes used for?

Reynolds: Windermere is used intensively for all kinds of recreational activities; it also supports salmonid fish populations. Blelham is used for sport fishing, but is not heavily angled. Crose Mere has been proposed as a national nature reserve and activities on that lake are restricted: the main uses are watering cattle and coarse fishing (fish caught are returned). Although the fish population of Crose Mere has not been well studied, similar glacial moraine lakes in the area have a high level of fish production, mostly perch and their predators, pike. I should emphasize that phosphorus does not kill lakes but may greatly disturb the balance of organisms living in them (for instance, one could not successfully stock Crose Mere with trout).

Alexander: That is a very important point.

Nicol: What do you mean by saying that Crose Mere is productive—productive in algae, productive in fish? To me, the word productive implies something useful.

Reynolds: I regard productive as meaning ecologically productive at each trophic level; whether the growth can be harvested or cropped is a different matter. Any system which has a high capacity for producing fish is productive in an applied way as well as an ecological way.

PHOSPHORUS IN ONTARIO LAKES AND RIVERS

Brydges: Relevant to this discussion is our experience with phosphorus in the Ontario lakes and rivers. Ontario has 250 000 inland lakes and borders on four of the five Great Lakes. The lakes are used extensively for fishing and
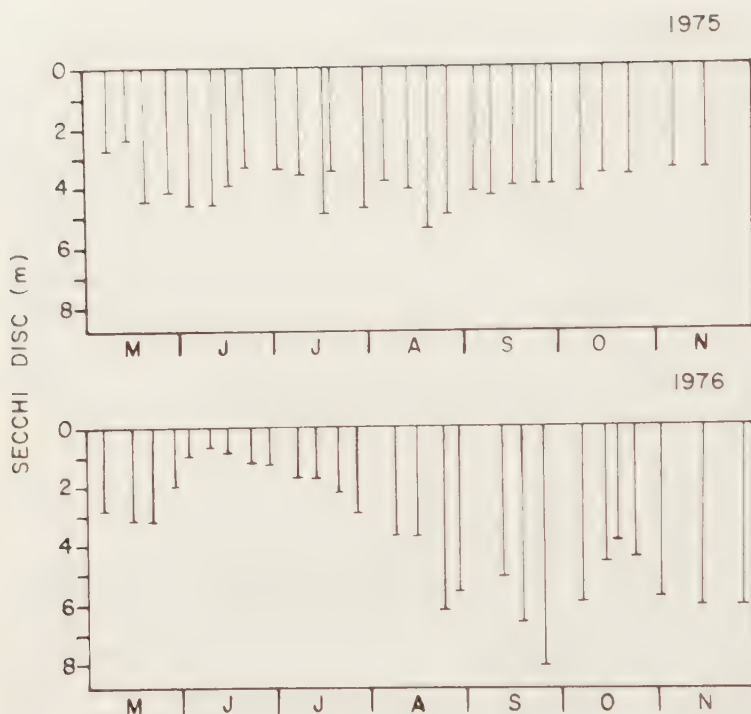
FIG. 1 (Brydges). Secchi-disc depths measured 1975 and 1976 in Gravenhurst Bay (mid-lake station) (from Dillon *et al.* 1977).

recreation (by Ontario residents as well as by many tourists). Some commercial fishing is done, particularly in the Great Lakes. Many lakes are located in the Precambrian Shield and have clear, soft water. The extensive development of summer cottages around the lakes (more than 200 000 dwellings) affects several thousand lakes to different degrees. These cottages (generally, second homes) are used mostly during the summer although winter use has increased since the introduction of the snowmobile.

As the Ontario Ministry of the Environment has overall responsibility for the control of pollution in Ontario and is also involved in environmental management, often in conjunction with the Ministry of Natural Resources, it has been concerned with the environmental aspects of phosphorus for many years.

In the mid 1960s, many lakes in North America suffered from the effects of accelerated eutrophication, or overfertilization by nutrients from man's activities: dense algal growths, poor clarity of water and low oxygen concentrations in the bottom waters. Lake Erie, the most famous example, was
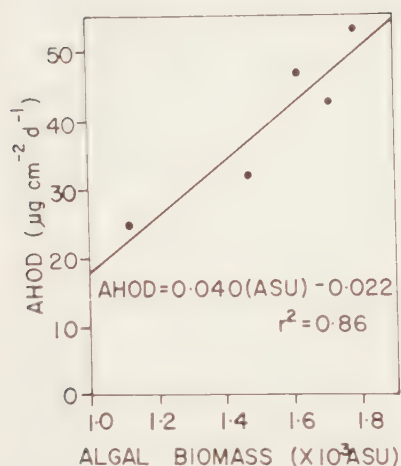
Fig. 2 (Brydges) Relationship between areal hypolimnetic oxygen deficit (AHOD) and mean algal biomass during the ice-free period in Gravenhurst Bay for 5 years (Table 2) (from Dillon *et al.* 1977).

claimed to be a dead lake and people often implied that many other lakes would follow the same path to destruction unless this accelerated eutrophication could be halted and reversed.

There was considerable controversy about the causes and controls of excessive algal growth, but many people felt that phosphorus was a key element in both promoting and controlling algal growth. 'Phosphobia', as one might call it, reached its climax in 1969 with a report to the International Joint Commission (Report 1969) which recommended that phosphates be replaced in detergents and that phosphorus should be removed from municipal and industrial effluents at waste-treatment plants. The report also called for control of phosphorus coming from agricultural sources. The recommendations were supported by subsequent work (Valentyne *et al.* 1970) which indicated that removal of phosphates from sewage eliminated excessive algal growth. Two questions remained: would removal of phosphorus (1) prevent eutrophication elsewhere and (2) reverse the effects in lakes such as Lake Erie which was already eutrophic?

In spite of some doubts amongst scientists, the Canadian Government issued regulations to reduce the phosphorus content of household laundry detergents: first, to 8.7% P by August 1970 and, secondly, to 2.2% P by December 1972. These dates were generally met by industry. (The State of Michigan also limited phosphorus to 8.7% in 1971.) The Ontario Government

began a programme of phosphorus removal at waste-treatment plants which now includes 183 plants with a total hydraulic capacity of 8.6×10^8 gal/d (about 3.9×10^9 l/d)—i.e. 87% of the total capacity of all communal treatment systems in the province.

After such an effort, has the programme been a success? The answer is an unqualified yes.

TABLE 1 (Brydges)

Morphometric and hydrological data for Gravenhurst Bay (Dillon *et al.* 1977)

Surface area (km²)	4.13
Mean depth (m)	7.6
Maximum depth (m)	15.8
Volume (m³)	3.14×10^7
Drainage basin area (km²)	38.9
Water replenishment time (yr)	1.8

Gravenhurst Bay. This bay (see Table 1) at the southern end of Lake Muskoka, about 130 km north of Toronto, is a major recreational and resort area for Ontario. It has received the secondary effluent from the sewage-treatment plant in Gravenhurst (population 6000) for many years. Removal of phosphorus at the sewage-treatment plant began in late 1971 and reduced the total amount of phosphorus in the effluent by 75% and the total phosphorus loading to the bay by 60% from the original loading of 2.4 g m⁻² yr⁻¹. The results are shown in Table 2. As the phosphorus concentration decreased, the algal population decreased and the water clarity (as measured by the Secchi-disc depth) increased.

The value of the programme was underlined by an incident in 1976. A new treatment plant was put on-line in late 1975 but, owing to teething problems, phosphorus was not removed. Secondary effluent was discharged all winter. A dense algal bloom appeared in the spring of 1976 with consequent poor clarity of water. Phosphorus removal at the sewage plant began in late May and, as Fig. 1 shows, the water clarity improved rapidly and significantly over the summer.

Oxygen concentrations below the thermocline are important for lake trout and other cold-water species of fish. Table 2 shows that as algal concentrations decreased, the rate of oxygen consumption (AHOD) decreased. This relationship (Fig. 2) provides a powerful tool for predicting the consequences for fish of any management practice which changes the number of algae, in particular any changes in phosphorus concentrations.
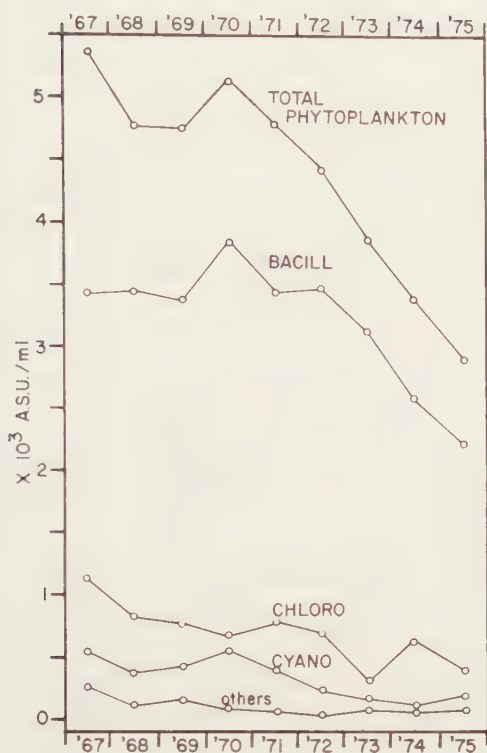
FIG. 3 (Brydges). Average biomass (as areal standard units/ml) of total phytoplankton and the dominant Classes in western Lake Erie between 1967 and 1975 at the Union Water Treatment Plant: BACILL, Bacillariophyceae; CHLORO, Chlorophyceae; CYANO, Cyanophyceae (from Nicholls *et al.* 1978).

Western Lake Erie. As the thrust for the phosphorus control programme came from problems in Lake Erie, what happened to that lake? Since 1967 the Ministry of the Environment has collected phytoplankton samples weekly from water intakes along the Great Lakes. Nicholls *et al.* (1978) have summarized the data for the near-shore areas of western Lake Erie. Fig. 3 shows the total phytoplankton and composition over nine years: note that the reduction in the amount of phosphorus detergents started in August 1970 and that the algal population started to decrease in 1971. The phosphorus concentration decreased by 40% from a 1967–1970 average of 62 mg/l to an average of 37 mg/l in 1976. Although these results do not necessarily reflect the conditions in the entire lake, they do indicate that a programme for the removal of phosphorus, which will eventually affect the whole lake, will improve the quality of the water.

TABLE 2 (Brydges)

The mean total amount of phosphorus (P), total inorganic nitrogen (TIN), organic nitrogen (TON), nitrogen/phosphorus ratio (TN/TP) (by weight) and chlorophyll a concentrations. Secchi disc* depth, and algal biomass from May to October, and areal hypolimnetic oxygen deficit (AHOD) in Gravenhurst Bay, 1969–1975 (Dillon et al. 1977).

Year	[P] (mg m⁻³)	TIN (mg m⁻³)	TON (mg m⁻³)	TN/TP	[chl a] (mg m⁻³)	Secchi (m)	Algal biomass (ASU ml⁻¹)	AHOD (mg cm⁻²d⁻¹)
1969	42	65	384	11.1	10.6	2.6	1780	0.053
1970	39	77	427	13.9	5.1	3.1	1620	0.047
1971	52	88	527	14.7	13.8	1.9	3620	
mean	44	77	446	13.2	9.8	2.5	2340	0.050
1972	35	144	383	17.8	8.1	3.1	1410	0.032
1973	33	163	399	18.3	6.9	3.2	1470	0.043
1974	25	188	356	24.8	5.0	2.7	1710	0.025
1975	20	257	320	35.2	5.0	3.9	1120	

* The Secchi disc is about 10 cm in diameter. It has four equal segments marked alternately black and white. The clarity of the water is recorded as the depth at which the disc is no longer visible.

Other lakes. As phosphorus has been removed in more treatment plants over the past few years, its concentrations have decreased in the receiving waters in several areas such as the Ottonabee River near Peterborough. It is still too early to evaluate the effects on water quality in these areas but they are being monitored.

One potential source of phosphorus to the many lakes with cottage development is seepage from the septic-tank tile beds. These beds are often located in shallow soil over bedrock and drain towards the lakes. A major study is in progress to quantify this effect but no firm conclusion has been drawn yet. However, in the event that this source of phosphorus must be controlled, a method for reducing the amount of phosphorus leaving the tank to the tile bed has been developed, in which alum is added to the septic tanks (Brandes 1976). With the proven effectiveness of the control of algal growth by the removal of phosphorus this alum treatment offers good insurance for the protection of water quality in many lakes already with extensive development.

Rivers. Rivers in Ontario also suffer from the effects of excessive plant and algal growth. It appears that phosphorus is also the key element in the control of plants in flowing water. Wong & Clark (1976) have measured the growth of *Cladophora* as a function of the internal and external phosphorus concentration. They determined that for phosphorus concentrations greater than 60 $\mu g/l$ growth was light-limited; at less than 60 μg P/l the maximum growth rate was limited by phosphorus. The fundamental concern over plants in river systems is their effect on dissolved oxygen concentrations during photosynthesis and respiration. If the plants grow too densely, respiration will reduce the dissolved oxygen below the acceptable values for fish and fish will die. Although this limit of 60 $\mu g/l$ has been determined, methods for defining an acceptable concentration to protect fish have not yet been developed.

In general, for each case where sufficient data have been collected, removal programmes have lowered concentrations of phosphorus in receiving waters. This lowering has in turn reduced algal growth and reversed eutrophication.

The benefit of phosphorus to surface waters. Phosphorus has been regarded as a pollutant in surface waters because increased algal growth decreases water clarity and spoils the look of lakes and rivers. Any benefits there may have been were lost in the concern over aesthetic deterioration. Now that methods to control this problem are available, some of our attention is turning to the beneficial effects of increased algal growth.

The population of fish that a body of water can support generally depends on the amount of primary productivity—or algal production. The clear Pre-

cambrian lakes are aesthetically pleasing and ideal for swimming but produce few fish: typical production in trout lakes is 1–2 kg fish ha^{-1} yr^{-1} (Fraser 1971) with typical total phosphorus concentrations less than 10 μg/l. In lakes with higher phosphorus concentrations more fish grow: the more enriched and shallow Kawartha Lakes in Ontario produce 4–5 kg fish ha^{-1} yr^{-1} with total phosphorus concentrations of about 25 μg/l (Anon 1976). Lawler *et al.* (1974) reported trout production of 70-313 kg/ha over a six-month growth period in eutrophic prairie ponds with up to 200 μg P/l. The phosphorus comes from run-off and is not deliberately added to the ponds.

As the phosphorus concentrations and fish production increase, a lake's aesthetic value and suitability for swimming decrease. However, the trade-off may be desirable in instances where fish production is the major use of the water body. The Kawartha Lakes almost have the best of both worlds, sustaining a good sport fishery but still having water of sufficient quality for extensive recreation.

Fish production cannot be related directly to phosphorus loadings or concentrations at present. Ryder *et al.* (1974) concluded that the general lack of success in relating primary production to fish yield is related to 'physiological and ecological limitations of the fish themselves'. One can still safely conclude that increased primary production through fertilization leads to increased fish production, but no quantitative relationship is known.

In a world where protein production will become increasingly important, Ontario's northern lakes appear attractive for fish production for two reasons. First, as with the Kawartha Lakes, at suitable levels of algal growth lakes can support many uses at the same time. This is seldom an option for land resources which almost always can sustain one use only—farm, park, housing, parking lot etc. Secondly, the land in the Precambrian and other northern areas cannot produce much protein whereas aquatic algae can take full advantage of long summer days to generate considerable primary productivity. Lakes are the potential farms of the north. The economic return from fish production in prairie ponds was 2.5 times greater than for an equal area of wheat (Weatherley & Cogger 1977).

Perhaps of particular interest to this symposium is the fact that phosphorus can be recycled in lakes in anoxic conditions. Although this is regarded as a negative aspect when trying to reverse eutrophication, it may be a phenomenon worth exploiting to improve the efficiency of use of phosphorus. I am not aware of a method of recycling phosphorus on land.

The Ontario Ministry of the Environment has been conducting fertilization experiments as part of reclamation studies on acid lakes near Sudbury. Experimental lakes with pH values about 4.5 and devoid of fish were neutralized

to near pH 7 with calcium hydroxide and carbonate. Total phosphorus concentrations were 2–5 µg/l. It was unlikely that such low phosphorus concentrations could support enough fish production to make liming of lakes economically feasible even for a sport fishery where the economic 'value' of the fish is greater than for food.

The addition of phosphoric acid to one lake (not enough to alter the pH), which raised the total phosphorus concentration from 2.5 to 8.1 µg/l, increased the growth of algae and zooplankton (see Table 3). The total amount of nitrogen and inorganic nitrogen in the water decreased (see Table 4). This change has not been fully explained and indicates the complicated nature of the effects of fertilization.

These data reveal that fertilization increased standing stock to the second trophic level even though data such as those for nitrogen were somewhat unexpected.

The results are encouraging support for the idea of increasing fish produc-

TABLE 3 (Brydges)

Effects of fertilization on Middle Lake Ontario (Scheider & Dillon 1976)

	Pre-fertilization	Post-fertilization
Total phosphorus (mg/m^3)	2.5	8.1
Chlorophyll a (mg/m^3)	1.1	2.4
Phytoplankton (ASU/ml)	143	703
Zooplankton (l^{-1})	0.64	2.32
Benthos (m^{-2})	96	138

TABLE 4 (Brydges)

Total nitrogen (TN) and total inorganic nitrogen (TIN) in treated lakes (Dillon *et al.* 1977*b*)

Lake	Year	Treatment	TN/mg m^{-3}	TIN/TN (%)	
Middle	1973	None	610	460	75
	1973/74	Base additions	667	482	72
	1975	P additions	485	255	53
	1976	P additions	469	175	37
Hannah	1973	None	900	780	87
	1974	None	720	590	82
	1975	Base additions	810	590	73
	1976	P additions	530	250	47
Lohi	1973	None	304	180	59
	1974	Base additions	195	97	50
	1975	Base additions	252	81	32
	1976	None	202	69	34

tion by deliberate fertilization of soft-water lakes in this climate and, as I have identified the need for such studies, our work is continuing.

van Wazer: You ascribe the success of the programme to action on the Canadian side of the Great Lakes. How much of the phosphorus that enters this area of Lake Erie comes from the American side and how much was the total reduced?

Brydges: The flow of the Detroit River keeps most of its material to the Detroit side of the lake and the Windsor (Canadian) side is somewhat separated in practice. Our study focused on the Windsor side.

Alexander: Of the phosphorus loading to the area 40% comes from the City of Detroit. This is flushed through to the south end of the western basin of Lake Erie, so effectively isolating the western basin on the northern shore. So Dr Brydges' figures do reflect the effects of the Canadian programme.

Brydges: I object strongly to the concept of trophic limits, as used by Dr Griffith, Mr Alexander and others in this symposium; namely that once phosphorus concentrations in a lake exceed Vollenwider's eutrophic limit (Vollenweider 1968) one does not worry about it. A great disservice to limnology was the introduction of the terms mesotrophic, oligotrophic and eutrophic. Once one lowers the trophic state of a body of water below one of these arbitrary limits, people sigh with relief but the fact of the matter is that the problems of chlorophyll, phosphorus and so on in water form a continuum. It may be that Lake Erie will not return to a non-eutrophic state. Maybe we don't want it to—after all it is one of the most important fisheries in North America. I can understand the reasons for and much validity in the concerns about removing phosphates from detergents but I wish people would stop using the conclusion that Lake Erie will still be above Vollenweider's eutrophic limit as a defence for continuing to add phosphorus because this conclusion is completely erroneous.

Griffith: The point is, what is the intended purpose for a body of water, in this case Lake Erie?

Brydges: In the short term, one should only try to reduce phosphorus to the lowest feasible concentration.

Griffith: Taken to its extreme that means that one should distil the water!

Brydges: But, within the realms of economic feasibility, we have shown in Ontario that the removal of phosphate at sewage-treatment plants and also from detergents does work for a large geographical area.

Griffith: I agree that the terms used for trophic state are horrible terms: no two limnologists agree on what eutrophic means. On the other hand, a mass of data has been accumulated and, if you do not accept Vollenweider's data, whose do you accept?

de Oude: May I suggest that we use the word 'hypertrophic' indicating 'excess food giving too many algae' (Golterman 1975). The pragmatic and probably most useful definition is: water quality that somebody does not like. This definition allows the water manager, responsible for a reservoir or lake, to set his goal. That goal may have to be (and certainly will be for parts of Belgium, Denmark, The Netherlands and the UK) an eutrophic lake–but in these cases eutrophic being a desirable condition. Let us reserve the word hypertrophic to describe the nuisance situation.

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The dissipation of phosphorus in sewage and sewage effluents

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Abstract Of the 41 kt of phosphorus reaching the sewage works in England and Wales 15 kt is removed in sewage sludge and the remainder is disposed of to rivers. 60% of the sewage sludge is now used as fertilizer and this proportion will no doubt increase in the future. The total use of sewage sludge, however, represents only about 5% of the current annual usage of artificial phosphorus fertilizer.

At present there is no general economic incentive to make better use of the phosphorus in effluents. Phosphorus removal is expensive—about 2–3 pence/m³. If all the sewage effluents in England and Wales were to be so treated the cost would be about £100–150 million annually, that is about 50% of the present costs of sewage treatment. In certain cases, but rarely in the UK, phosphate is removed, not to conserve phosphorus but to minimize the problems it creates in the environment. The phosphorus removed has little value as fertilizer.

Alternative methods of using the phosphorus in effluents by the production and harvesting of crops of algae or aquatic plants have so far proved uneconomic. However, these methods need to be reviewed periodically as they may in the future become economically more attractive, especially in warmer climates where plant growth can be maintained throughout the year.

In recent years much attention has been focused on the role of sewage, as a source of phosphorus, in the eutrophication of waters. My purpose in this paper is to put the flow of phosphorus in sewage into the environment into perspective and to discuss ways of reducing it, along with estimates of costs, implications and likely benefits.

PHOSPHATE CONTENT OF SEWAGE

An adult normally excretes 1.3–1.5 g of phosphorus* per day (Jenkins & Lockett 1943) and disposes of a further 1.2 g/d derived from synthetic deter-

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* Throughout this paper all values of phosphorus or phosphate are quoted as P.

gents (Water Pollution Research Laboratory 1970). Together these account for almost all the phosphorus in domestic sewage. Most sewages consist of mixtures of domestic and industrial wastes and the latter may contain phosphates derived mainly from metal-finishing processes.

Using these data for England and Wales for 1970 when the population whose sewage was being treated was about 43 million, one can calculate that the annual release of phosphorus in sewage was about 41 000 tonnes (41 kt). This then is an estimate of the total quantity of phosphorus in domestic sewage arriving at the sewage works. Once there, it is treated and some of the phosphorus is retained by the solids, known as sewage sludge, and the remainder, mainly in solution, remains in the effluent which is discharged into rivers.

The Working Party on Sewage Disposal (Ministry of Housing and Local Government 1970) estimated that in 1970 the total production of sewage sludge in England and Wales was about 1.1 Mt dry matter and that this contained about 15 kt of phosphorus (J. D. Swanwick, personal communication, 1977). In round figures, then, 40% of the phosphorus in sewage is retained by the sludge and 60% remains in the effluent. These figures compare well with the direct observations of Harkness & Jenkins (1958) who found that 37–38% of the phosphorus was removed at two works but, at a third where high concentrations of metals were present, the removal was 68%. Jenkins & Menar (1967) examined the kinetics of phosphorus assimilation in the activated sludge process and concluded that the maximum removal of phosphorus as a result of biological processes would not exceed 20%.

SEWAGE SLUDGE

In England and Wales about 20% of the sewage sludge produced is disposed of into the sea; about 60% is used as fertilizer and the remainder is dumped on land tips (Department of the Environment 1977).

To put in perspective the value of sewage sludge as a source of phosphorus fertilizer one should compare the phosphorus content with the 150 kt of artificial phosphate fertilizer used annually in England and Wales. Sludge thus represents at most 10% of this usage and probably less, as it is doubtful that all the phosphorus is available to plants; estimates of its availability vary between 50–70% (Water Pollution Research Laboratory 1972).

Of the 40% of sludge which is not applied as fertilizer only a small percentage is so toxic as to be unfit for this purpose. Why then is not more used?

In seaside towns, which contain about 12% of the UK population, it is undoubtedly much cheaper to dispose of crude sewage direct to the sea even

when, as is the case now, sea outfalls have to be much longer to ensure that beaches are not contaminated.

A second and more important reason has been some reluctance on the part of farmers and gardeners to use sludge. This is partly on aesthetic grounds and partly as a result of extensive field trials during and just after World War II, the results of which were not encouraging (Bunting 1963). Since 1961 work on the use of liquid digested sludges, which incidentally have little smell, has given much more promising results (Drew 1962; Coker 1966). An increase in the dry-matter content of grass and barley similar to that produced by equivalent amounts of nitrogenous fertilizer was found although the production of protein was rather less (Water Pollution Research Laboratory 1972). By meeting the nitrogen requirements of crops, these liquid digested sludges probably slightly exceed the crops' needs for phosphorus (Water Pollution Research Laboratory 1972).

In addition to providing nitrogen and phosphorus digested sludges also go some way to meeting the organic and calcium carbonate needs of the soil (Water Pollution Research Laboratory 1972). This is an added bonus in view of the concern expressed at the developing deficiencies of these constituents by the Agricultural Advisory Council on Soil Structure and Soil Fertility (Ministry of Agriculture Fisheries and Food 1970).

These recent studies on the successful use of sewage sludges, in conjunction with the Agricultural Development and Advisory Service's recommendations for maximum safe limits for the addition of some metals contained in sludges to soils (Ministry of Agriculture Fisheries and Food 1971), should go a long way towards promoting their more widespread use and thus aiding a beneficial recycling of phosphorus resources.

SEWAGE EFFLUENTS AND EUTROPHICATION

About a third to over a half of the phosphorus arriving at sewage works passes into rivers. The concentration of phosphorus in effluents varies; values from 3 to 14 mg/l have been reported by Owens & Wood (1968). These authors observed phosphorus concentrations of 0.17–0.73 mg/l in a reach of the Great Ouse river and estimated that over 90% was derived from sewage effluents. A similar range, 0.13–1.51 mg/l, has been reported for the River Thames near Oxford (Youngman 1975), of which 90–95% can be accounted for by sewage effluents.

Algae need little phosphorus for growth. Mackereth (1953) estimated that 1 μg P/l would support about 16×10^6 cells of *Asterionella formosa* per litre, a population density which would be sufficient to make the treatment of a water

containing it difficult. The quantity of phosphorus needed to support comparable quantities of algae varies with the species. Vollenweider (1968) quotes data suggesting that *Microcystis* sp., a blue-green alga, needs more than 2.5 times as much phosphorus as *Asterionella formosa* for comparable growth (see Table 1). He also presents information indicating that different species need different phosphorus concentrations to achieve their maximum density.

TABLE 1

Phosphorus requirements of various species of algae (from Vollenweider 1968)

Species	Minimum P requirement (µg per unit cell volume [mm³])	P concentration (µg/l) at which maximum density achieved
Asterionella	0.2	≤ 10
Fragilaria	0.2–0.35	≤ 50
Tabellaria	0.45–0.60	
Scenedesmus	> 0.5	> 500
Oscillatoria	> 0.5	> 3000
Microcystis	> 0.5	

Thus waters receiving quite small volumes of sewage effluents are likely to have phosphorus contents well in excess of those necessary to support large algal crops.

It is now generally accepted, particularly for static waters, that at phosphorus concentrations in excess of 10 µg/l considerable algal growths may occur which can interfere with the various uses of water. In view of this, much effort has been directed towards reducing the concentration of phosphorus in sewage effluents. In Sweden and Canada a portion of the phosphate in synthetic detergents, which in the UK may contain up to 10% phosphorus but in Canada may exceed 13% (Department of the Environment 1971), has been replaced by the sodium salt of nitrilotriacetic acid (NTA). It is said that NTA can replace 70% of the polyphosphates in synthetic detergents but, as polyphosphates account for only 46% of the phosphorus in sewage in the UK, such a replacement would only effect an overall phosphorus reduction of 32%. The benefit of such a reduction in terms of algal growth is likely to be small and this would be gained at the expense of introducing a strong complexing agent into the environment. Although work has shown that efficiently-run sewage works should remove most of the NTA (Bouveng *et al.* 1968; Swisher *et al.* 1967), it is inevitable that some will get into rivers where it could affect the ecosystem by complexing trace metals. Indeed it could even

enhance algal growths, as iron complexed by ethylenediamine tetraacetic acid (EDTA) is often added to algal cultures and initiates good growth when all else has failed. In addition to complexing metals in the environment NTA could also complex metals when domestic and industrial effluents are mixed and thus carry toxic materials through the sewage works into rivers. In view of the likely small benefits, the replacement of phosphates by NTA should be viewed with some caution.

An alternative to replacing the phosphorus in detergent is its removal from the sewage effluent. Between 66 and 98% has been removed by precipitation by lime or salts of aluminium or iron (Bayley 1970). In view of its low cost, ready availability and good settling properties, lime is probably the most attractive agent (Bayley 1970). Present costs for phosphate removal are in the region of 2–3 pence/m^3 of effluent treated (R. Gregory, personal communication 1977). As the total daily flow of sewage effluent in England and Wales is about 14×10^6 m^3, treatment to remove phosphorus would cost an additional £100–150 million annually, a sum which is about 50% of the present cost of sewage treatment.

The sludge from phosphate removal processes appears to be a good source of fertilizer. Cooke & Williams (1970), however, state that the phosphate produced by the lime process is so insoluble that the sludge is best regarded as lime containing a little more phosphate than usual.

Attempts to use the nutrients in sewage effluents by the production of algae and plants have been made. The crops have been used as a source either of animal feed (Burlew 1953) or of fuel (Benemann *et al.* 1977)—in the latter case by their anaerobic decomposition to methane. So far none of these ventures has been successful as the costs of harvesting and processing the crops have been too great. The situation, however, needs to be kept under review as it is possible that in warmer parts of the world, where active plant growth can be maintained throughout the year, these uses may eventually become economic.

DISCUSSION

Although potential phosphorus production from sewage sludge is only about 5–7% of the annual commercial fertilizer usage there are advantages to be gained by exploiting it: first, to conserve resources; secondly, to reduce costs of sewage treatment. Recent work has gone a long way towards demonstrating the value of sewage sludge as a fertilizer and there now seems no reason why, given a vigorous marketing policy by the Water Authorities, farmer and gardener alike should not be convinced that sludge is a useful fertilizer. The five-fold increase in the UK price of phosphorus fertilizers

resulting from entry into the European Economic Community and the rising cost of oil should also encourage the use of sewage sludges. It must not be forgotten, however, that 60% of the sludge produced in England and Wales is already applied to the land and even use of all the sludge would only make a small economy in the overall usage of phosphorus. We shall have to look to other sources to make greater savings. For example, Cooke (1976) has reported that of the 198 kt of phosphorus produced by farm animals in the UK two thirds is spread by grazing animals but of the remaining 65 kt produced by animals in intensive-rearing units the costs of removing and spreading are greater than its value as a fertilizer. This source of phosphorus, representing almost half the present artificial fertilizer usage, needs to be used more efficiently. It is an area where subsidies could possibly be applied to ensure the proper use of natural resources.

The position with regard to the conservation of phosphorus in sewage effluents is much less clear than for sludges. The use of effluents for the production of crops of algae or aquatic plants which are subsequently used as animal feed or fuel has so far failed on economic grounds. On the other hand, to recommend generally that phosphorus be removed from all effluents on the basis of the problems it creates in the environment would be costly and cannot be justified.

Before it can be recommended that phosphorus removal be practised it is necessary to establish that phosphorus is the factor causing eutrophication and to draw up a budget with major sources identified and quantified. With this information it can be seen how much the phosphorus loading of the water will be reduced by removing the phosphate from effluents. If algal growth is limited by phosphate then any percentage reduction in phosphorus loading should be matched by a similar decrease in algal activity. However, reality is not as simple as this because the problems associated with eutrophication vary with the use of the water and the use is not just affected by the quantity of algae but also by the species. The best way to illustrate this is by a few examples.

The eutrophication problem at Lough Neagh (Northern Ireland) is only associated with the large crops of blue-green algae although the lake supports large crops of other algae (Gibson et al. 1971). Despite the fact that growths of these blue-green algae occur regularly they rarely cause problems. This is because Lough Neagh is a wind-swept body of water and, as a consequence, the conditions conducive to blue-green algae forming blooms—that is, bright, calm weather—rarely occur. In 1967 such weather conditions coincided with a large crop of blue-green algae which bloomed; extensive scums were taken on the gentle breeze and concentrated on the leeward shores. This led to much

reaction from the commercial fishermen, anglers, industrialists and the public. However, as Lund (1970) pointed out, a similar phenomenon occurred in 1910 and the problem could reflect bloom and weather conditions coinciding rather than recently increased nutrient loadings.

Recommendations have now been made to remove the phosphate from the effluents of 12 sewage plants discharging to the lough at a capital cost of £150 000–200 000 and an annual running cost of £300 000 (Department of the Environment, Northern Ireland 1975). Depending on which of the estimated phosphorus budgets for the lough is correct this should bring about a removal of between 20 and 50%. If algal production is directly limited by phosphorus, the removal of phosphorus should lead to a similar reduction in algal crops and, as algae are the primary producers, ultimately in the fish production. I still have some doubts, however, that this expected reduction will be sufficient to overcome the type of problem that occurred in 1967.

It does not necessarily follow that increases in phosphorus will bring about an immediate increase in algal production. Lund (1973) has reported that in the south basin of Lake Windermere phosphorus concentrations have increased six-fold in the past 29 years without any major change in the phytoplankton, whereas in Blelham Tarn similar increases have produced marked changes (see Reynolds, in this volume).

Plots of maximum phosphate concentrations against maximum chlorophyll concentrations (Sakamoto 1966; Lund 1970; Collingwood 1977) show the general trend of increased growths with increased phosphorus concentration (Fig. 1). However, at any particular concentration of phosphorus the amount of chlorophyll may vary by as much as 10 times and such variability could be sufficient to make the difference between whether eutrophication was a problem or not.

Several instances have been reported showing the value of phosphate removal in arresting eutrophication (Edmondson 1972; Thomas & Wildi 1975). Many of these cases demonstrate how little phosphorus is needed to change an oligotrophic—that is, nutrient-poor water—to a eutrophic water. A good example of this, Blelham Tarn, has been described (Lund 1973). Over the past 20 years or so improvements in the water supply and disposal of sewage from a population of less than 100 people have resulted in all the community's waste phosphorus being discharged to the tarn. Previously waste water had been disposed of in septic tanks. The winter concentrations of phosphate in the tarn now reach 10 µg/l, some five times greater than 20 years ago, and this increase has had a dramatic effect on the algal production. Although this relatively small increase has had such a large effect in Blelham Tarn, a similar change in some of the highly eutrophic waters of the South of England would pass virtually unnoticed.
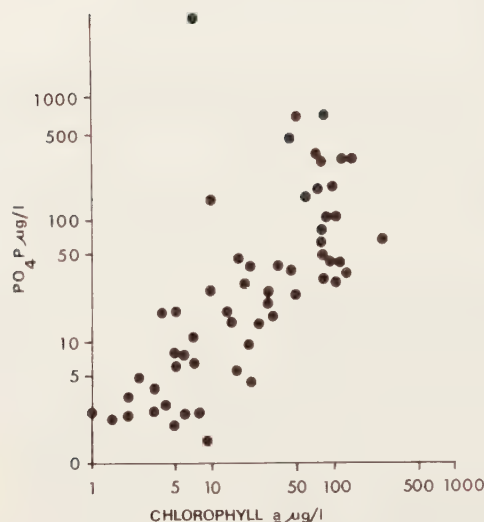
Fig. 1. Maximum annual chlorophyll a concentration plotted against maximum annual phosphate phosphorus concentration for some British lakes and reservoirs.

Conversely, although one could relatively easily remove the phosphorus from the inflows to Blelham Tarn and, in the main, restore the lake to its original status, this could not be done so easily for very eutrophic waters. Farmoor reservoir in the Thames Valley is an example of such a water which has a phosphorus loading of about 5 g m^{-2} yr^{-1} (Youngman 1975) and even if 95% of this were removed the new loading of 0.25 g m^{-2} yr^{-1} would still be sufficient to make it eutrophic although then, no doubt, different species would dominate the phytoplankton.

I have described elsewhere (1977) the effects different species of algae have on water-treatment processes. In a waterworks, where alum coagulation, sedimentation and rapid sand filtration were used, whereas one algal species created severe filtration problems, four times the biomass of another species was treated with little difficulty. Also I warned that in some cases phosphate removal could lead to more severe filtration problems as the algae which cause these difficulties may be favoured by lower phosphorus concentrations.

The purpose of these few examples has been to illustrate the complexities of the eutrophication problem and to show that, although phosphorus, along with other nutrients, is an important factor in eutrophication, it is by no means the only factor. This, combined with our imperfect understanding of the factors controlling algal populations and species succession, makes it impossible for general recommendations to be made for the removal of phosphorus from sewage effluents; such recommendations would not only be costly but in many instances would have little or no benefit.

Lund (1974) summarized the position well and I shall conclude by quoting him:

"The eutrophication problem is not the same everywhere. It is doubtful whether the best remedy for one lake or one lake region is the best for all. Phosphate enrichment may produce unwanted changes in one lake but will not do so in another. Moreover opinions differ about which substances are the most harmful. It seems reasonable that each lake or lake area should be considered separately bearing in mind the general, though still imperfect, knowledge of eutrophication. Then it can be decided whether remedial measures are necessary, what they might be, whether they are acceptable on economic or other grounds and whether legislation is necessary to implement them."

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Discussion

Nielen: Another factor that should be taken into account is dilution. Even though advanced sewage-treatment plants may remove 90% or more of the phosphorus, it is the absolute concentration of phosphorus that is important. This dilution factor varies greatly but it is, at least, 10-fold (in some cases 25-fold). For instance, lowering of the phosphorus concentration by advanced sewage-treatment to 1 mg/l would mean a maximum concentration after dilution in surface waters of 0.1 mg P/l below which phosphorus is definitely growth limiting.

Collingwood: The concentration at which phosphorus is growth-limiting is very much less than 0.1 mg/l; less than 0.01 mg/l is a more likely figure (see p. 232). One must investigate each specific site to identify and quantify all the inputs of phosphorus into that system and, having done that (a formidable task), one can then make a rational decision about whether the removal of sewage-derived phosphate is likely to be successful in reducing troublesome algal growths. At the 20th (1977) Congress of the Society of International Limnology in Copenhagen an example was quoted where the phosphorus budget had not been worked out fully. The phosphorus had been removed from the sewage but the whole operation was not successful because the reduction of the total phosphorus loading to the lake was not as great as was expected.

R. J. P. Williams: You quoted a figure of 46% for the amount of phosphate in sewage from detergents. Is that figure peculiar to the UK or does it apply to other countries?

Collingwood: It is fairly general although it varies a little from place to place. For example, some countries use more phosphorus in their detergents; up to 13% (as P) in North America compared with up to 10% in the UK.

Nielen: The phosphorus content of heavy-duty European detergents is lower: it varies between 5 and 10% P. As far as the contribution to sewage is concerned, about 50% is an acceptable average figure. But locally there may be great differences in the figures: in rural areas the percentage will be much lower and in densely populated areas where there is no erosion from the land the percentage may be slightly higher than the average.

R. J. P. Williams: Can we put absolute numbers to these percentages? How much phosphate enters the water systems, not just by sewage but from run-off etc?

Collingwood: In rivers not subject to pollution by sewage the phosphorus concentrations will be low and derived largely from soil erosion; in rivers with a high sewage loading over 90% of the phosphorus may be derived from the sewage (see p. 231).

Bowman: Our estimates for the UK (see elsewhere in the volume and Bowman 1977) for the amount of phosphorus in sewage coming from detergents indicate a figure nearer 60% of the total. This figure was arrived at by two independent estimates.

Nielen: Limnologists in Germany analysed the area of Bodensee and determined that about 40% of the phosphorus came from detergents, about 40% from faeces and about 20% from fertilizers (the German Chemical Society 1977).

Griffith: What is the Environmental Protection Agency's figure for detergents in the USA?

Alexander: That depends on the area, because of the different State limitations on detergents. Of the total loading to Lake Erie from the US side 50–60% of the phosphorus in sewage comes from detergent but about 65% of the total phosphorus coming into the lake derives from land run-off (and that raises the question of availability) and about 35% comes from sewage.

Collingwood: Percentages can be misleading; we must bear in mind the concentration.

Loughman: With regard to the diatoms, besides having a high requirement for phosphate, several species have a specific requirement for boron. Have borate concentrations been measured?

Collingwood: Detergents also contain boron and sewage effluents may contain 1–2 mg/l of boron. Many waters are probably not deficient in boron. Silicon regularly limits the growth of diatoms. For example, almost every year the growth of diatoms in Farmoor, a eutrophic reservoir near Oxford storing River Thames water, is terminated by the lack of silicon. If the limitation of algal growth by phosphorus were so clear-cut, we should have a case to lay at the door of the detergent manufacturers.

Reynolds: The conclusions of Lund's studies (1950) which showed that silica became limiting at certain concentrations should be modified in view of the adjustments in concentrations of other materials and the complex interactions between them, and between silicon and light. Algae seem to have so regulated themselves that they take up no more silicon than their immediate requirement. When silica is available, growth can begin. But when the amount of silica is reduced to the limiting concentration during growth the rate of growth immediately falls because the cells cannot construct new siliceous skeletons. This contrasts with the limitations on growth of phosphorus and nitrogen, for instance, when the growth rate is directly related to the concentration of the nutrient available.

Collingwood: Silicon limits the standing crop rather than the rate.

R. J. P. Williams: Would these water systems be disadvantaged if silicon was added to them?

Collingwood: Yes; such an addition could lead to enhanced growth of diatoms.

R. J. P. Williams: So, besides metals which are beyond our scope in this symposium, we should bear in mind silicon and boron in relation to phosphorus.

Arthur: If I may comment on the use of sewage effluent, I believe that if it were offered at a suitable price this water might find an important use as cooling water. That is perhaps a more positive way of looking at the problem than worrying simply about the recovery of phosphorus. In the UK, process water is in extremely short supply.

Collingwood: Unfortunately distribution of the water would be extremely expensive. A rough estimate for laying large mains in the UK is 20 pence (mm diam.)$^{-1}$ m^{-1}. To transport large volumes of water mains up to 1200 mm in diameter are used which cost about £250 m^{-1}.

Nielen: How successful has been the Thames Water Authority's idea of delivering sewage sludge free of charge to farmers?

Collingwood: This service was only announced in August 1977 so it is much too early to judge its success, but the response to a similar service offered by the Yorkshire Water Authority suggests that it is likely to be successful. The economic situation favours the use of sewage sludge; the cost of phosphate fertilizer has increased five times since the UK joined the European Economic Community.

Reynolds: With regard to harvesting algal growth, blue-green algae have their own built-in harvesting mechanism: every so often they rise to the surface and accumulate on the shores. These growths can be used: Professor Pirie has described (1976) how people in Chad collect and eat *Spirulina*. Also, Soviet scientists have developed a plant which takes blue-green algae off Ukrainian reservoirs and is then extracted for amino acids (see Bogdanova *et al.* 1975).

Pirie: At what pH is that?

Reynolds: I don't know.

Pirie: The lakes near Mexico City, the growths from which are harvested commercially, have a pH of about 10.

van Wazer: What is the water content of these algae?

Reynolds: The proteinaceous fraction of natural phytoplankton suspensions is in the order of 1×10^{-6} and the algal blooms may concentrate this by 3–4 orders, but even then perhaps only 1% is solid.

van Wazer: The main cost of harvesting would then be the drying.

Nicol: How feasible would it be to treat the effluent from the sewage works by a concentration process such as pumping through membranes or reverse

osmosis? The concentrated effluent might subsequently be used as irrigation water and the purer water returned to the water courses.

Collingwood: As most of the phosphorus in effluents is in solution, filtration will not remove it. Filtration of water is expensive; it could cost almost as much as the 2–3 pence/m³ quoted for the removal of phosphorus. Reverse osmosis can be used to remove phosphorus from water; it is a very efficient process but is several times more expensive than chemical removal processes.

The concentration of boron in effluents can be sufficiently high to render the water unsuitable for the irrigation of boron-sensitive crops (Waggot 1969).

Nicol: When lime is added to sewage effluents does the cost lie in the filtration of the sludge?

Collingwood: The most expensive step is separation of the sludge after the lime has been added. Again, the problem is one of harvesting.

Brydges: Whatever the percentage is, it is a fact that removal of phosphorus from sewage effluents vastly improves the quality of the receiving water. A lot of phosphorus from other sources comes in as sand, silt, debris and so on, and is not available. Most of the phosphorus in sewage is available and the algal growth is greater than with an equal amount of phosphorus from other sources.

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Balance sheet for phosphorus in the UK

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Abstract A balance sheet for the inputs, uses and outputs of phosphorus in the UK economy has been drawn up. The major import is fertilizer, amounting to about 200 kt P per year. After fertilizers, the other imports (in kt P) are in animal feeds (63), detergents (38) and human food (14). The major outputs are sewage (50), animal excreta (26) and refuse (21); soil losses are about 20 kt. The flow-paths for phosphorus through humans, animals and plants are described. The discrepancy of about 210 kt P/yr is explained by the fact that the amount of phosphorus in the soil increases each year by almost as much as the amount of fertilizer phosphorus added. In view of UK dependence on this imported resource it is suggested that priority is given to work which might eventually have some practical application in preventing or reversing the immobilization of phosphorus in the soil.

About two years ago I became involved in considerations of national agricultural strategy, at a time when the United Kingdom was particularly concerned with import saving. The cost of phosphorus had gone up by a factor of five and the political stability of the country which is the main source of phosphorus for the UK and Europe was not good. So it seemed a good idea to have a look at the problems for agriculture that might be posed by curtailment of phosphorus supplies.

The first task was to obtain a quantitative picture of phosphorus in the UK economy. The results to date are shown in Fig. 1 in which the quantities represent thousands of tonnes (kt) of phosphorus per annum. These quantities relate to the 1973–74 period. Although later data are available, the data were selected deliberately to avoid changes due to marked price alterations in 1974 and later. A full description of the sources of data and the calculations which enabled Fig. 1 to be constructed are given in the Centre for Agricultural Strategy's (1978) publication.

This description of the quantities of phosphorus in UK agriculture together
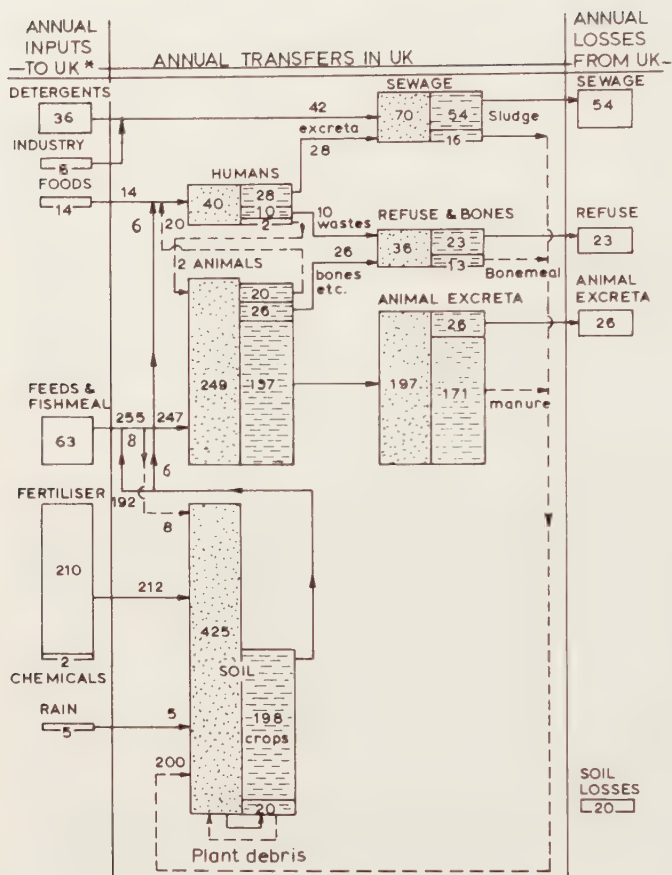
Fig. 1. UK phosphorus economy: all figures refer to thousands of tonnes P, rounded to the nearest thousand. Data are based on 1973 except where otherwise as stated in text. *With the exception of rain the annual inputs refer to imports of phosphorus (in raw materials, foods and feeds). Dotted boxes show inputs, dashed boxes show outputs.

with a consideration of the problems which might arise as a result of curtailment of phosphorus imports leads to the following conclusions.

(1) CONSUMPTION AND SUPPLY OF PHOSPHORUS

The cost of UK imports of rock phosphate has risen from £16 million in 1973 to about £50 million a year from 1974 onwards. The probability of future increases in price and the possibility of reduced availability on world markets make an up-to-date geological/economic study of UK phosphorus deposits desirable.

(2) PROCESSING ROCK PHOSPHATE

Although total world resources of phosphorus are vast, some of the more easily accessible high-grade ores are being depleted. This makes it imperative to consider (i) the use of lower-grade ores for processing and (ii) the direct use in agriculture of less highly processed sources of fertilizer.

(3) USE OF PHOSPHORUS

There is no alternative to phosphorus as a fertilizer, but there are possible substitutes for phosphorus in detergents. Continued investigation of replacements for polyphosphates in detergents is consistent with efforts to reduce pollution of water courses and, at the same time, reduce UK imports of phosphorus.

(4) RECOVERY OF PHOSPHORUS

The application of sewage sludge to agricultural land should continue to be encouraged. Recovery of phosphorus from sewage is technically feasible but the cost is high in relation to the fertilizer value alone. It would seem to be in the national interest to reduce the input of phosphorus *to* sewage (through exclusion of phosphatic detergents) rather than to invest effort on its removal *from* sewage.

There is considerable scope for avoiding irrecoverable loss of phosphorus from land through loss in drainage water of phosphorus from animal excreta. The need for maximum conservation of plant nutrients and minimum pollution of watercourses is likely to make the use of animal excreta an increasingly important consideration in the future choice of farming systems.

(5) PHOSPHORUS IN SOILS

To estimate accurately the future requirements for phosphorus we need to know the expected removal by crops, the unavoidable losses *from* the soil and the retention of phosphorus *by* the soil. Although there are some gaps in our knowledge about losses from the soil, the greatest need is for further knowledge of the extent and rate of conversion of phosphorus from available into unavailable forms in different soils. The high rate of immobilization of phosphorus suggests that priority should be given to research that might eventually have some practical application in preventing or reversing the immobilization of phosphorus in soil.

(6) PHOSPHORUS AND CROPS

There is a need to study the ability of plants to extract and use nutrients from the soil. The selection of crops or cultivars for their ability to absorb phosphorus and/or to use absorbed phosphorus efficiently, is an example of plant research which might have strategic implications. Knowledge is also needed about the role of residual phosphate in the attainment of high crop yields.

(7) USE OF PHOSPHORUS FERTILIZER

UK farmers are using about 175 kt of fertilizer phosphorus a year, at a cost (in 1975–76) of about £150 million. In 1975, application of phosphorus to sugar beet and, to a lesser extent to winter wheat, exceeded the recommendations made by the Agricultural Development Advisory Service; savings should be effected. On many farms where soil concentrations of phosphorus have been built up by previous fertilization, it should be possible to reduce the amount of phosphorus applied over a whole rotation to maintenance levels only. The effects of any such reductions would need to be checked by regular soil testing. Systematic monitoring of soil concentrations of phosphorus in all parts of the UK would be of strategic value.

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Discussion

Kabbaj: Professor Larsen (pp. 20, 93) qualified Professor Williams' diagram (p. 2), saying that only 10% of the phosphate in soil reached the plants but your figures, Professor Bowman, suggested that output is nearly 50% of the total input.

Larsen: That figure of 10% is the extra amount of phosphorus taken up by a crop after fertilizer has been added to the soil. This estimate gives an answer to the question of how much fertilizer phosphate is transferred to the plants. But Professor Bowman's calculation shows a different picture, namely that one third to one half of the phosphorus added to the soil is taken up, but much of that comes from what is already there. We cannot strictly compare the two figures. If one used ^{32}P, one could compare them.

Bowman: If one were able to measure the amount of phosphorus in the soil reservoir and add that to the total input of 425 kt, then the 198 kt removed in crops might represent 10% of the total input plus the reservoir of phosphorus. In other words we are saying that the soil contains roughly a further 1.5 Mt of phosphorus.

Pirie: But at the end of the year that reservoir of phosphorus is still there.

Kabbaj: Even so, some of the phosphorus in the reservoir is usable.

Larsen: Professor Bowman, your data are most impressive; Fig. 1 contains many more details than any I have seen elsewhere. Although individual figures are different for Denmark, we share a common problem, namely that the concentration of animal husbandry makes nonsense of the recycling of phosphate. In extreme cases, some arable farms in Denmark have no farm-yard manure but others have embarrassingly large quantities and the soil is the only place where it can be put. This excess creates a fertility problem—as a consequence of the amounts of nitrogen as well as phosphorus. Farmers in such a position may spread 200–300 t/ha although the normal amount of farmyard manure applied is 20 t/ha but they do not seem to derive any benefit from this excess of phosphorus that they add to the soil.

With regard to soil testing one condition is that the advisory test should be quick and expressed by a single number. In a study of soil as a source of phosphorus we must, however, take into account four parameters: quantity, intensity, rate, and geometry (i.e. diffusion). They cannot be reduced to one figure, as seems to be demanded of those in the advisory business. We must also remember that soil is extremely heterogeneous on both a macro- and a micro-scale. The 'pH of the soil', for instance, has no meaning: an average figure of, say, pH 7.2 may hide the fact that in one spot it may be 5, but a few millimetres away where some organic matter is decomposing, producing am-monia, the pH may be 9. Similarly, statistical examination will reveal that the sampling error is massive—about ± 30–40%. That error plays havoc with any figures derived from soil testing, because for example within one field the soil can be phosphorus-deficient in one corner yet rich in phosphorus in another. Consequently farmers apply a blanket dressing in order to take account of the deficient areas.

Tinker: I agree with Professor Larsen that the diagram is too optimistic in implying that all the 171 kt of phosphate in animal excreta goes back onto the soil uniformly. It does not; it goes back in all sorts of inefficient ways, with considerable maldistribution.

To take up Professor Larsen's last point about why farmers persist in putting too much phosphorus on the soil, I suggest that continued persuasion of farmers will succeed in changing their practices. For example, the recom-

mended amount of phosphate for sugar beet has been falling for some time as more information became available, but only recently have farmers accepted this decreased recommendation (Church & Webber 1971). I have considerable sympathy for farmers, because we tell them what to do but they have to spend the money; they depend on us being right. Although the yield of a crop may increase as the addition of fertilizer increases, it flattens off at higher levels and the amount of profit may decrease slightly as more fertilizer is added. The negative slope of the profit curve is often smaller at high rates of addition than the positive slope at lower rates and so, even if the farmer trusts the recommendations, he knows that, if he under-fertilizes his loss may be considerable, whereas if he over-fertilizes he is only losing a small amount. Because of the different potential losses it is easy to see why farmers are on the side of overaddition rather than underaddition of fertilizer.

Bowman: We have allowed for the point you raised, Dr Tinker. We arrived at the figure of 26 kt for the loss of phosphate through animal excreta by calculating how much of the livestock is intensively farmed and how much is likely to be on the farms not attached to land where the muck can be spread, and what proportion of the animals are grazing animals.

Shaw: In many parts of the world animal excreta are used as fuel. As we have an energy problem as well as a phosphorus problem, would it be worth trying to persuade people to return the dung to the soil rather than burning it?

Bowman: If excreta are burnt, the residue can still be used on the land and presumably the phosphorus is then more available. If the animal excreta are used in digestion systems to produce methane gas I do not know what happens to the residue but it can probably be put on the land. I have no information on the form of the phosphorus in the residues.

Larsen: When faeces are burnt, hydroxyapatite becomes more crystalline and less reactive. When biogas is made much phosphorus is transformed from mineral to organic forms in bacterial tissues.

Shaw: Is the phosphorus in animal excreta more available than that in mineral phosphates?

Larsen: Phosphate in faeces is colloidal calcium phosphate of the apatite form. It is finely divided and a slow-acting source of phosphorus. Over a six-year period of crop rotation it will supply as much to the crop as chemical fertilizer does.

Shaw: Does the use of animal excreta alter the structure of the soil?

Bowman: The evidence is conflicting but the latest view at Rothamsted is that application of raw farmyard manure to the soil apparently has structural effects which are helpful to crop growth (Cooke 1976).

van Wazer: Composting manure builds up the amount of polyelectrolytes

so stabilizing the soil when the composting is properly done (see, e.g., Satriana 1974; King 1911).

Larsen: We are shying away from the $64 000 question that Professor Bowman posed, namely how can we liberate the reserve of phosphate which has accumulated in the soil and is just lying there until somebody can find a means of getting it back into the cycle.

R. J. P. Williams: We shall concentrate on that question and examine it later (see pp. 289-301).

Nielen: The German Chemical Society's Phosphate Study Group (1977), which includes three members from industry (the remaining 12 are non-industrial experts on fertilizers etc.), has constructed a similar flow-chart for the use of phosphate in the Federal Republic of Germany but includes nearly 100 different flow-paths. The input figures which are now available ought to lead to more research in certain topics rather than to legal decisions.

Arthur: It may be appropriate for a member of the fertilizer industry to make a few comments about the amount of phosphorus used by farmers. Fisons is undertaking work to try to understand better the state of soil phosphorus and the availability of soil phosphorus to plants: these factors are basic to sound recommendations to farmers. The usual approach adopted by soil chemists to help to elucidate soil phosphorus availability is to try to make phosphorus balances between what is applied, what is taken out by crops and what remains in the soil. They recognize four forms of phosphorus combination in soil, which they term organic, solution, labile and non-labile (see Fig. 1). Only phosphorus in solution is available directly to plants and it can be
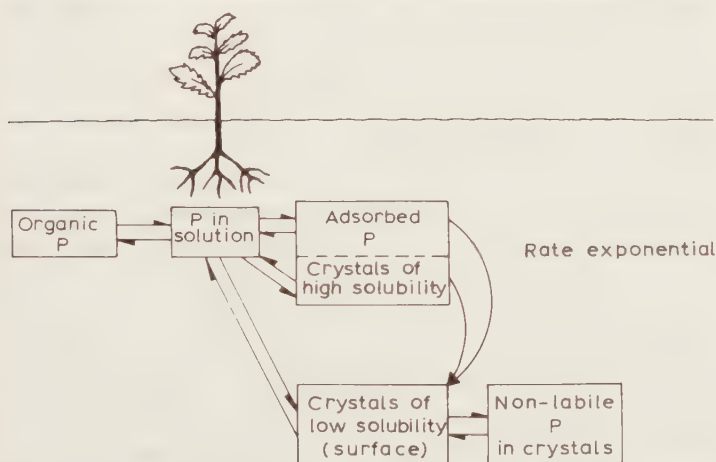
FIG. 1 (Arthur). The four forms of phosphorus in the soil: organic, solution, labile (adsorbed and crystalline), and non-labile.

replenished from the labile form as it is taken up. The key question is, what constitutes the labile form? In Fig. 1 labile phosphorus is represented in two boxes and is defined as follows: (1) it is derived from several sources; (2) part is chemically *active*, changing to less-soluble forms and so falling in concentration with time; (3) part is chemically *stable*, and its contribution does not change in the medium term; (4) the amount can depend on removals. With these concepts of labile phosphate and the states of combination of phosphorus in soils, we have begun to develop a mathematical model for the use of phosphorus by arable crops; this work (mainly due to J. D. Whitear) has

$$fRP = PA + PS \tag{1}$$

$$fRP_1 = PS + rF_1 + PAe^{-kt_1} + F_1(1 - r)e^{-kt_2} - CP\left(\frac{PA + F_1}{PA + PS + F_1}\right) \tag{2}$$

not been published before. The basis of this model, given in equation (1), states that the amount of resin-extractable phosphorus RP is made up of the two forms of labile phosphate: active labile phosphate PA and stable labile phosphate PS; f is a conversion factor from p.p.m. to kg/ha. The quantity of labile phosphate declines with time. Equation (2) indicates how, at the end of one year, the amount of resin-extractable phosphorus is made up of the stable labile phosphate, the remaining fertilizer phosphate (F_1 is the amount of fertilizer phosphorus added and r is the fraction of fertilizer phosphorus expected to be resin-extractable when the exponential decay is complete) and the partly decayed active labile phosphate (k is the decay coefficient, t_1 is the time between soil samples and t_2 is the time from addition of fertilizer phosphorus to second soil sample) less the phosphorus removed by the crop (*CP*). This model has been tested in several arable situations, in particular to calculate the amount of resin-extractable phosphorus in several instances with and without addition of fertilizer phosphorus. This model is still being developed but the agreement so far between calculated and observed values is good, and it seems to be a promising step towards better-planned phosphorus fertilization. The practical application of the model depends on the ability to predict the rate of loss of availability in different soils. We need a simple way of doing that; isotopic dilution (of which Professor Larsen was an early exponent) is somewhat complicated. Professor Larsen's early work showed that it should be possible to forecast this decay coefficient (*k*), and a routine method of doing this more simply than the isotopic dilution method is being worked on. We may be at the beginning of a better understanding of this decay process for labile phosphorus and I hope that this will help us to a more quantitative appreciation of phosphorus fertilization.

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The use of phosphate in detergents and possible replacements for phosphate

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Abstract About 5% of the total phosphate mined worldwide is used in detergents. The chemical form in which phosphate is used in detergents is predominantly pentasodium triphosphate (PSTP). The most significant feature for the use of PSTP in detergents is its ability to form soluble and strong complexes with calcium and magnesium ions. This provides a strong synergism with regard to detergency when PSTP is used in combination with synthetic surfactants. Other important features of PSTP are its ability to disperse dirt in the washing solution, its weak alkalinity, its crystalline form when dry (which enables production of crisp powders) and, last but not least, its toxicological acceptability. The development of PSTP for use in detergents has a history of over 25 years.

In certain areas of highly developed countries where effluents from major centres of population can reach stagnant surface waters a rapid increase of eutrophication of these surface waters is observed. Phosphates are being recognized as one of the essential nutrients contributing to the eutrophication and detergents are one of the many sources of phosphate discharged to the environment. This is now causing demands for reduction in or even banning of the use of phosphates in detergents.

Major research projects and some practical approaches to meeting these demands are described. The potential environmental impact of removing phosphate from detergents remains, however, doubtful, as it has been demonstrated in Sweden that phosphate removal by sewage treatment is the most effective measure to control phosphate discharges. This makes the case of phosphates in detergents an example of how science and technology can become entangled with politics.

The problem connected with the use of phosphates in detergents is neither one of limited resources of raw materials nor one of misuse of the products; it is purely the possible environmental consequences of the discharge of phosphate after its use. The more we search for alternative materials to replace detergent phosphates the more we become convinced about the almost ideal combination of properties and cost offered by the phosphates

used in detergents. The apparent disadvantage in its discharge to the aquatic environment stems from the fact that phosphate is a nutrient and adds to eutrophication.

WORLD CONSUMPTION OF DETERGENT PHOSPHATE

The total amount of phosphates used in detergents world-wide is about 1.8 $\times 10^6$ ton (expressed as P_2O_5). This is of the order of 5% of all the phosphate mined around the world (Fig. 1). Most detergent phosphate is used in the USA and Europe, but this distribution is now being affected by major restrictions and bans on the use of phosphates in detergents in parts of North America and expected restrictions in parts of Europe.
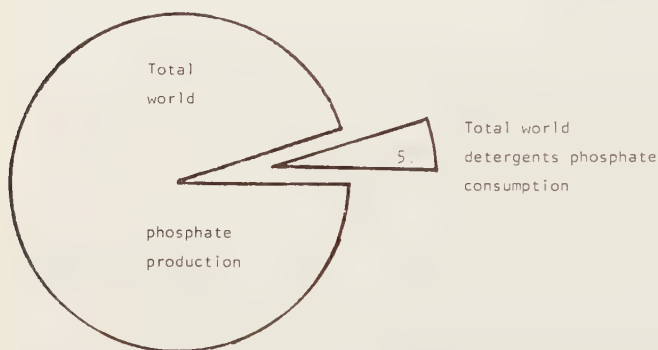
Fig. 1. Proportion of the total world production of phosphate used in detergents.

SPECIFIC PROPERTIES OF DETERGENT PHOSPHATES

The phosphate salt commonly used in detergents is pentasodium triphosphate: $Na_5P_3O_{10}$. The substance is manufactured with a high degree of purity by heating monosodium and disodium orthophosphate in a molar ratio of 1:2 (reaction 1). The triphosphate is a crystalline substance which can form a hexahydrate and it is not hygroscopic in normal ambient conditions.

$$NaH_2PO_4 + 2Na_2HPO_4 \rightarrow \left[O - \overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}} - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}} - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}} - O \right]^{5-} 5Na^+ \quad (1)$$
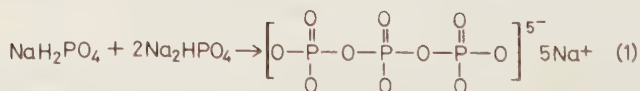
In aqueous solution the triphosphate forms strongly bound and soluble complexes with calcium and magnesium ions—in other words, it sequesters the ions responsible for the hardness of water. The basic ability of modern laundry detergents to remove dirt is provided by the combination of this

sequestering capacity of triphosphate with the surface active properties of synthetic surfactants. The surfactant acts synergistically with the triphosphate; neither agent alone will give the same detergent performance as in combination. Table 1 summarizes some of the properties of the triphosphate. The triphosphate prevents greying of fabrics by keeping the dirt suspended in the washing solution. It also prevents the deposition of insoluble calcium and magnesium salts on textiles and in the washing machine. The mild buffered alkalinity provided by the triphosphate supports the detergency. The crystallinity of the dry material is an important asset for the manufacture of free flowing powders. Last but not least, triphosphate is toxicologically entirely acceptable.

TABLE 1

Some properties of pentasodium triphosphate, $Na_5P_3O_{10}$

It forms soluble and strong complexes with Ca^{2+} and Mg^{2+} ions.
It disperses particulate dirt.
It provides mild buffered alkalinity.
It is non-hygroscopic.
It forms crystalline anhydrous and hydrated salts.
It is toxicologically acceptable.
It has relatively low cost.

These specific properties of triphosphate are especially important for the washing of fabrics. Fabric-washing products may contain from 20% up to 65% of triphosphate, depending on whether they are designed for fine wash, heavy-duty purpose or medium-temperature main wash (Fig. 2).

In most European countries and North America the tonnage of fabric-washing products represents about half the total detergent market. Consequently triphosphate is a major ingredient in the most important segment of the detergent market. Detergents for mechanical dishwashing may contain up to 60% triphosphate but the total consumption for this purpose is relatively small. The use of triphosphate in other detergent products is negligible.

THE ALLEGED DISADVANTAGE OF PHOSPHATE

After a washing operation the wash liquors are sent down the drain. In most developed countries this drain enters an organized sewerage system, which receives all the aqueous wastes and residues normally discharged by communities. With or without treatment these combined effluents, which are rich in all the essential nutrients that contribute to eutrophication, may eventually reach rivers and lakes. Since several other speakers in the
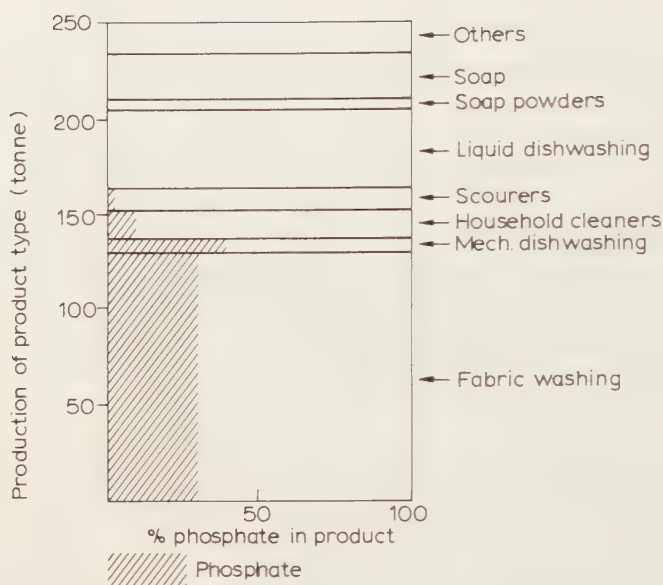
Fig. 2. Use of pentasodium triphosphate in detergent products in the Netherlands in 1975. The shaded area represents the percentage of triphosphate in the product.

symposium focus on this subject we shall limit our comments to listing the conclusions which we expect will be drawn from these papers and which are pertinent to the problem of detergent phosphate:

. man-made eutrophication is a regional problem of stagnant waters depending on the hydrological situation in relation to the size and activity of the population in the water-catchment area;

. phosphorus is a key element in man-made eutrophication of inland waters;

. the discharge of phosphorus from man's activities is more readily controllable than the discharge of any other essential nutrient contributing to eutrophication;

. domestic effluents in densely populated areas contain up to 75% of the total phosphorus released to the aquatic environment and up to half the phosphate in these effluents may come from detergents;

. the most effective measure to control discharge of phosphate from human activities to the aquatic environment is removal of phosphate from sewage and the appropriate treatments are available to do this (Fig. 3);

. the removal of phosphate from detergent will have little, if any, effect on controlling man-made eutrophication.

Only the authorities in Sweden have accepted these conclusions in their entirety and initiated a national policy of phosphate removal by sewage

| Treatment | % removal | P conc |
	10 20 30 40 50 60 70 80 90	effluent ppm
I pre–settling	BOD / P	⟩ 5
II pre–settling + chem. precipitation	BOD / P	0.4–0.8
III pre–settling + biol. oxidation	BOD / P	⟩ 5
IV pre–settling + biol. oxidation + chem precipitation	BOD / P	0.1–0.5
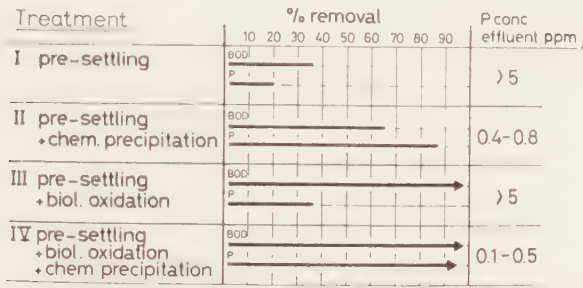
FIG. 3. Efficiency of biological oxidation (measured as BOD, five-day biological oxygen demand) and removal of phosphorus during sewage treatment (the phosphorus concentration in the effluent is given in p.p.m.).

treatment. The beneficial results from some 600 treatment plants built since 1970 on the water quality of Swedish lakes fully justify this policy. On the other hand, the authorities in certain states of the USA have neglected the last two statements in the list and have banned the use of phosphate in detergents. The environmental impact of these bans remains doubtful. In some areas in Europe, namely Germany, Switzerland and the Netherlands, the authorities are adopting a policy of removal of phosphate from sewage, but in addition significant reductions in the use of phosphate in detergents are expected.

SOME APPROACHES TO THE REPLACEMENT OF PHOSPHATES IN DETERGENTS

The detergent and chemical industries in the USA and Europe have been working for more than 10 years to find appropriate replacements for triphosphate in detergents. The criteria that any substitute for triphosphate in detergents must satisfy are that it must be:
effective in terms of product performance;
safe for man and the environment; and
within acceptable cost limits.
In spite of the enormous expenditure by industry on this search (which may now exceed £100 million), a compound that is satisfactory in all aspects for everyone concerned has not been found. Nevertheless, let us look at some of the successes and limitations of the work done so far.

Nitrilotriacetic acid

When detergent phosphates began to be regarded as a problem, prevailing opinion favoured the replacement of triphosphate by sodium salt of nitrilo-triacetic acid (NTA). NTA strongly sequesters calcium and magnesium ions

and its detergent performance is similar to that of triphosphate. It is available in commercial quantities and, in terms of cost and performance, is comparable with triphosphate. The acute toxicity of NTA is acceptable and it is appreciably biodegradable during sewage treatment. Substantial financial commitments had been made for the manufacture of NTA for use in detergents in the USA when it was suggested by Dr S. Epstein (to the Sub-Committee on Air and Water Pollution of the Committee on Public Works in the USA in May 1970), on superficial evidence, that NTA caused cancer. Consequently, the US Surgeon General urged the soap and detergent industry in the USA immediately to withdraw NTA from detergents. In spite of major investigations the carcinogenicity of NTA has not been established to the satisfaction of the US health authorities. In Canada, however, the authorities tolerate the use of NTA in detergents but, nevertheless, they keep the concentration of NTA in rivers, lakes and drinking water under strict surveillance.

A further objection to NTA is its ability to form stable and soluble complexes with heavy metals. Such complexation could mobilize heavy metals from river sediments and this mobilization could be detrimental in some polluted rivers. The chances for extensive use of NTA in detergents remain minimal in the present climate where even the slightest doubt is turned into an overriding negative.

Sodium carbonate–silicate

In the early 1970s the detergent industry in the USA reluctantly replaced the triphosphate in detergents sold in certain areas by a mixture of sodium carbonate and silicate. In these areas the use of phosphate in detergents had been prohibited by law and the federal authorities had recommended that NTA should not be used. No other substitute was available.
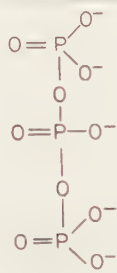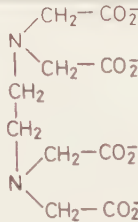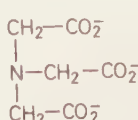
Although sodium carbonate–silicate mixtures are less efficient than triphosphate, they help detergency by precipitating calcium and magnesium ions and by their alkalinity. The build-up of precipitates, however, on fabrics and in the washing machines is undesirable. In European fabric-washing conditions (temperatures up to 100 °C in washing machines with built-in heaters), the use of carbonate–silicate formulations would even more severely impair the appearance and life of both textiles and washing machines.

New soluble sequestrants

Hundreds of organic substances, previously known as well as newly synthesized compounds, have been investigated for their ability to replace

TABLE 2

Structure, ability to complex calcium ions (expressed as log K_{Ca}, the equilibrium constant for the calcium complex) and biodegradability of pentasodium triphosphate (PSTP), enthylenediamine-tetraacetic acid (EDTA) and nitrilotriacetic acid

Property	PSTP	EDTA	NTA
Structure	(structure diagram)	(structure diagram)	(structure diagram)
Log K_{Ca}	6.0	11.6	6.5
Biodegradation	(Hydrolysed)	No	Yes

triphosphate in detergents. Some details of a major Unilever research project may illustrate the approach.

For detergency the ability to form strongly bound and soluble calcium and magnesium complexes is a basic requirement for a substitute for triphosphate. NTA and EDTA (Table 2), which both form such complexes, were taken as model substances but candidate substitutes could contain only carbon, hydrogen and oxygen, and no nitrogen. The typical sequestering properties of NTA and EDTA are based on the presence and steric arrangement of the
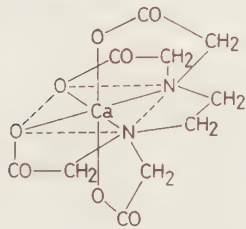
FIG. 4. Structure of the Ca–EDTA complex.

carboxy groups and the participation of the nitrogen atom in the formation of the complex (Fig. 4). The number of carboxy groups and their steric disposition determine the binding forces for various metal ions.

We applied the following criteria in the initial screening programme for new substances: (1) the ability to complex calcium ions (expressed as log K_{Ca}, see Table 2) should be as near 6 (the value for the triphosphate) as possible
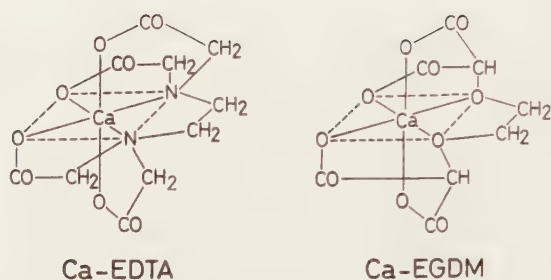
Ca-EDTA   Ca-EGDM

Fig. 5. Structures of the Ca–EDTA and Ca–EGDM complexes.

and not lower than 4 (which is of the order of the value for citrate, which makes only a slight contribution to detergency); (2) the compound should be rapidly and completely biodegraded in laboratory test conditions. Note that in this initial screening cost was not a criterion.

Tables 3–5 show various synthetic compounds with their log K_{Ca} values and performances in a biodegradation test. For each basis type of structure, the log K_{Ca} value increases with the number of carboxy groups until the target value of 6 is reached with four carboxy groups. Note that the structures of the calcium complexes of EDTA and EGDM (Fig. 5) are strikingly similar. This observation encouraged us but we were immediately frustrated by the lack of biodegradation of the acids with higher log K_{Ca} values. The results obtained so far suggested two options for further work: to develop further CMOS (see Table 3) which had the highest calcium sequestering power (log K_{Ca} 4.4) of those substances which passed the biodegradability screen; and to study further the biodegradability of those substances which met the calcium-sequestering target of log K_{Ca} = 6. Although we took up both options, we put more emphasis on the first.

TABLE 3

Structure, calcium-binding ability and biodegradability of three oxy-acids: oxydiacetate (ODA), carboxymethoxysuccinate (CMOS) and oxydisuccinate (ODS)

Property	ODA	CMOS	ODS
Structure	$CH_2-CO_2^-$ $\mid$ O $\mid$ $CH_2-CO_2^-$	$CH_2-CO_2^-$ $\mid$ O $\mid$ $CH-CO_2^-$ $\mid$ $CH_2-CO_2^-$	$CH_2-CO_2^-$ $\mid$ $CH-CO_2^-$ $\mid$ O $\mid$ $CH-CO_2^-$ $\mid$ $CH_2-CO_2^-$
No. of CO_2-groups	2	3	4
Log K_{Ca}	3.6	4.4.	5.8
Biodegradation	Yes	Yes	No

TABLE 4

Structure, calcium-binding ability and biodegradability of four ethylenedioxy-acids: ethylene glycol diacetate (EGDA), ethylene glycol acetate malonate (EGAM), ethylene glycol dimalonate (EGDM) and tartaric dimalonate (TDM)

Property	EGDA	EGAM	EGDM	TDM
Structure	$CH_2-CO_2^-$ $\|$ O $\|$ CH_2 $\|$ CH_2 $\|$ O $\|$ $CH_2-CO_2^-$	$CH{<}^{CO_2^-}$ $\|\quad CO_2^-$ O $\|$ CH_2 $\|$ CH_2 $\|$ O $\|$ $CH_2-CO_2^-$	$CH{<}^{CO_2^-}$ $\|\quad CO_2^-$ O $\|$ CH_2 $\|$ CH_2 $\|$ O $\|\quad CO_2^-$ $CH{<}_{CO_2^-}$	$CH{<}^{CO_2^-}$ $\|\quad CO_2^-$ O $\|$ $CH-CO_2^-$ $\|$ $CH-CO_2^-$ $\|$ O $\|\quad CO_2^-$ $CH{<}_{CO_2^-}$
No. of CO_2^- groups	2	3	4	6
Log K_{Ca}	3.6	4.8	5.7	7.1
Biodegradation	Yes	No	No	No

TABLE 5

Structure, calcium-binding ability and biodegradability of three oxydiacids: oxydiacetate (ODA), oxyacetatemalonate (OAM) and oxydimalonate (ODM)

Property	ODA	OAM	ODM
Structure	$CH_2-CO_2^-$ $\|$ O $\|$ $CH_2-CO_2^-$	$CH_2-CO_2^-$ $\|$ O $\|\quad CO_2^-$ $CH{<}_{CO_2^-}$	$CH{<}^{CO_2^-}$ $\|\quad CO_2^-$ $O\quad CO_2^-$ $\|\quad$ $CH{<}_{CO_2^-}$
No. of CO_2^- groups	2	3	4
Log K_{Ca}	3.6	5.1	6.1
Biodegradation	Yes	No	No

As we expected from its moderate ability to complex calcium, CMOS does not meet the high standard of detergent performance of triphosphate but this handicap is less apparent in washing conditions in the USA than in Europe. The short-term and long-term toxicity of CMOS appears to be entirely acceptable and biodegradation is rapid and complete. The estimated cost of producing CMOS is 1.5–2 times that for triphosphate. Processes for manu-
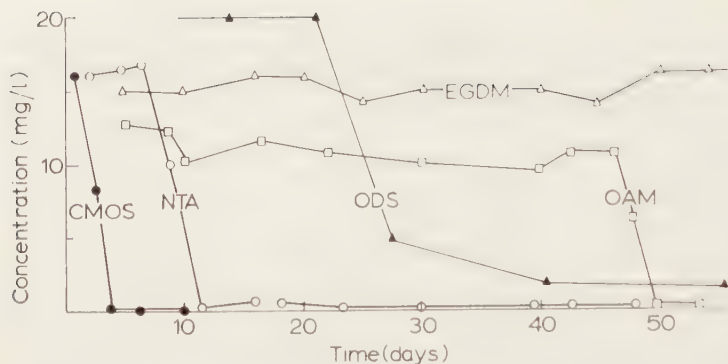
FIG. 6. Biodegradability of some organic complexing agents—CMOS, NTA, ODS, EGDM and OAM (see Tables 3–5).

facturing CMOS have been developed to a stage where commercial manufacture can be considered in the USA.

Further investigations into the biodegradation of the new substances with ability to complex calcium close to that of triphosphate focused in particular on acclimatization. In laboratory test conditions, with the test substances as the sole source of carbon, we observed rapid and almost complete biodegradation of oxydisuccinate (ODS, log K_{Ca} 5.8) after 3–4 week's acclimatization (Fig. 6). This result is encouraging but we now need to establish the relevance of this observation for practical situations in the environment.

Numerous publications in scientific literature and patents suggest that many others have been searching in the same area for new substances to replace triphosphate. The combined criteria of effectiveness, safety and cost compared with triphosphate have made this search extremely difficult and nobody seems to have found the ideal compound yet.

Zeolites

If phosphate in detergents cannot yet be completely replaced by an effective and safe substitute in the short or medium term, what about partial replacement? In this context much attention is being focused on the use of type A zeolites.

Crystalline zeolites (Fig. 7) are aluminosilicates consisting of a three-dimensional network of aluminate and silica tetrahedra linked to each other by sharing all oxygen atoms. Zeolites have already been in use for a long time as water softeners because of their ion-exchange capacity. Type A zeolites can
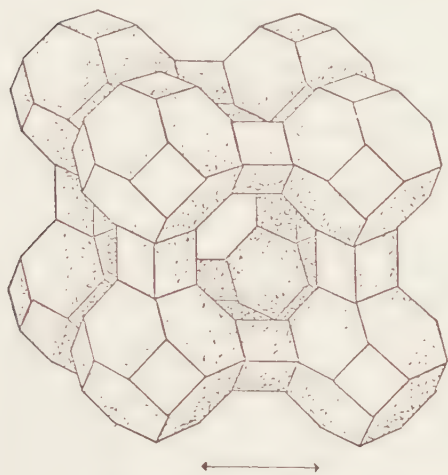
Fig. 7. Structure of a type A zeolite: pore size (indicated by arrow), 0.42 nm; α cages 1.14 nm.

bind calcium ions and, to a lesser extent, magnesium ions. This property enables them to perform, at least in part, the functions of triphosphate in detergents. In certain washing conditions up to 50% of triphosphate can be replaced by type A zeolites without too great a sacrifice of performance. At higher degrees of replacement, however, the facts that type A zeolites bind the ions responsible for the hardness of water less strongly than triphosphate does and that zeolites are insoluble in water become a handicap. Combinations of type A zeolites with other strong sequestrants of calcium and magnesium may, however, open up further opportunities for substitution of triphosphate.

With regard to human health aspects and potential environmental consequences type A zeolites seem to be entirely satisfactory, although some long-term studies are still in progress.

The technology for large-scale manufacture of type A zeolites is available but production facilities will need to be built. Some major detergent companies in Western Europe and the USA have announced that they will partially replace triphosphate by type A zeolites in their laundry detergents, provided that no health and environmental risk is indicated from the current safety investigations.

SUMMARY

Sodium triphosphate is vital to the high performance standards of modern synthetic fabric washing detergents. It offers a unique combination of detergent performance effectiveness, toxicological acceptability and cost.

Opponents of its use allege that it contributes to man-made eutrophication of stagnant inland waters. In spite of data which clearly demonstrate that appropriate sewage treatment is the most effective measure to combat man-made eutrophication, substantial political pressure has been applied against the use of phosphate in detergents, leading to bans on the use of phosphates in detergents in some areas. The detergent and chemical industries have been searching for more than 10 years for an appropriate triphosphate substitute. The specific properties of triphosphate, however, appear to be unique and no substitute is available today which will satisfy all the criteria. Science and technology are therefore struggling with politics on second-grade compromises.

Discussion

Nielen: Fig. 6 shows the rate of biodegradation of several potential substitutes for phosphate. I presume that these tests are run at 20 °C. However, at temperatures lower than 20 °C the rate of biodegradation of NTA decreases tremendously from 12 days and below 5 °C stops (Eden *et al.* 1972).

Gilbert: That is true, but practical experience in Canada (Prakash 1976) where NTA is used indicated that poor degradation at low temperature was not a major problem since warm flows of sewage and adjustments by plant operators compensate sufficiently for the low temperature. The concentrations of NTA in the environment have been low (a few µg/l) even during winter. Therefore, I hesitate before extrapolating conclusions from laboratory experiments to practical systems.

Brydges: A recent Task Force Report on non-phosphate detergent builders' to the International Joint Commission could find no evidence that NTA would create any obvious environmental hazards.

Nielen: Has the US Department of Health, Education and Welfare any plans for recommending NTA in the USA in the near future?

Alexander: As far as I know, there are no such plans. About five years ago the US Surgeon General *suggested* to the soap and detergent industry that they not use NTA, but NTA is not illegal in the USA. A report from the Great Lakes' Research Advisory Board (1976) (a joint board between Canada and the USA) recommends to the International Joint Commission that the use of NTA be continued in Canada and be considered in the USA. It claims that 'from the standpoints of both human health and the environment—fish and wild life—NTA is about as dangerous as peanut butter'. Whether the Surgeon General will change his mind remains to be seen but all the evidence adduced

so far after four years of study on the considerable use of NTA in Canada points to the absence of any problem (except in estuaries—of which there are not many in the USA and none in the Great Lakes district). I foresee no problem.

Bowman: Would there be any danger of using NTA when (as in the UK) river water is re-used several times for drinking? For example, the Thames is drunk by different populations seven times in 100 miles. Might NTA increase the concentration of metals in the water?

Gilbert: In the UK many sewage works operate on mixed domestic sewage and industrial effluents containing high loadings of heavy metals. At present these are largely taken up and held by the activated sludge or humus solids and, therefore, are not discharged to the receiving waters. The fear has been expressed that in such plants, if the removal of NTA were poor owing to adverse operational conditions, some heavy metals might be transferred into rivers.

Alexander: That has not been the experience in Canada, which has plants that treat both domestic and industrial sewage.

Gilbert: But the dilution in the Great Lakes is immense. As Dr Bowman said, in Europe some effluents are re-used six or seven times for drinking water; dilution is much less. Particular concern has been expressed in Germany about the Rhine which contains relatively high concentrations of heavy metals in the sediments and is an important source of drinking water.

Johnston: Another factor which should be mentioned is the diversity of laundry operations between North America and Europe. Generally speaking, these use liquor/load ratios of around 18 and 5 to 1, respectively. Consequently the waste-detergent solutions discharged to drains and reaching sewage-treatment plants are much more concentrated in Europe than in North America. In the UK, for example, there is the additional problem that many sewage works operate at near (or over, on occasion) design capacity, with consequently short residence times for the influents; added to this is Professor Bowman's point about the re-use of effluents. These facts are significant in the light of research at Imperial College, London (R. Perry & J. N. Lester, personal communication) on the biodegradability of NTA in a laboratory simulation of a continuous activated-sludge plant (modified Husmann apparatus). This showed that in hard water about 28 days were required for acclimatization of the sludge bacteria to NTA; in soft water acclimatization was much slower and more erratic. Moreover, even after acclimatization, the application of a shock load of NTA (double the normal concentration) to the system, such as is to be expected on wash days, led to serious stripping of heavy metals from the activated sludge by undegraded NTA which carried them through the system.

Brydges: Has that been demonstrated on a major plant?

Johnston: No; these were laboratory experiments.

R. J. P. Williams: Simple chemistry demands that nitrogen-containing compounds are kept out of any system for removing calcium and magnesium because they will always also chelate strongly the heavy metals. In this respect tripolyphosphate has an enormous advantage over NTA, and that is why most potential substitutes for this phosphate in detergents have been compounds containing carbon, hydrogen and oxygen only (see p. 259). For the same reason sulphur must be excluded. Any accident with a nitrogen-containing sequestering agent will surely mobilize cadmium, lead, copper and zinc. If NTA is biodegradable, that is lucky because basically it is bad material (from a chemical point of view).

Gilbert: A further disadvantage of nitrogen-containing compounds, particularly relevant when the water is re-used, lies in the fact that, on biodegradation, they contribute nitrate to the system. Not only is nitrate a nutrient but its presence in drinking water can lead to methaemoglobinaemia in infants. In some areas its concentration in drinking water is already approaching a critical level (Tucker 1974).

R. J. P. Williams: How soluble are the silicates that are added to detergents and do they increase the amount of mobile silicon?

de Oude: Zeolites are insoluble. They have been tested on several species of algae, including diatoms; no increase in algal growth was observed.

R. J. P. Williams: Certain organisms release compounds that can dissolve quartz (never mind these silicates) (see Nobel Symposium on *Biochemistry of Silicon and Related Problems* 1978). Any concern should focus especially on diatoms not just algae because I gather that the diatoms need the silicon whereas many algae do not need it essentially.

Nielen: These silicates are not always insoluble. At lower pH values, the insoluble sodium aluminium silicate (the zeolite) can be broken down into forms of silicate which are soluble for a certain time. Some silicates in detergents are initially soluble in water and then precipitate; even this process might be reversible.

Gilbert: Furthermore, used detergents are always discharged to domestic sewage and sewage effluents are likely to be already saturated with silica.

van Wazer: How long will zeolites persist in surface waters?

de Oude: Zeolites are to a large extent removed during sewage treatment. This has been demonstrated in plant experiments where mechanical plus biological treatment removed about 90%.

van Wazer: Is that with tertiary treatment?

de Oude: No, only precipitation and biological treatment. Also, zeolites

are not stable in water (Savitsky, in press): their crystal structure changes and they are converted into a precursor of kaolinite whereupon they lose their ion-exchange capacity. It is important to note that we are not dealing with complexing reactions (where orders-of-magnitude differences exist between the stability constants for different metals) but with ion-exchange reactions.

van Wazer: How long is the lifetime for this breakdown of ion-exchange capacity?

de Oude: The lifetime of zeolites in water is not known; for natural waters it is safe to say that it is less than a few days.

Johnston: In cases where sewage plants are overloaded surely the danger exists of zeolites being incompletely removed and some being carried through the treatment plant into the receiving water before they lose their capacity to complex metals?

de Oude: Any reaction of a zeolite with a metal results in an insoluble complex.

Johnston: Which, in adverse conditions, may be carried through into the effluent water.

Gilbert: Since the zeolites are insoluble, the adverse conditions which you propose would only pertain when there was inefficient settling of sewage solids. But at present the heavy metals are largely bound to the activated sludge or humus solids and in ideal conditions are substantially removed in the secondary settlers. Therefore, in such poorly operating plants the heavy metals will already be present in the effluent, associated with the suspended solids. The addition of zeolites is not, therefore, likely to make the situation worse.

de Oude: Adding this insoluble zeolite to the influent of a sewage-treatment plant can only be beneficial since any metal taken up would then be in an insoluble form.

Johnston: I still maintain that there is a considerable risk that they would be carried through the plant, in this instance as solids, since the use of zeolites in detergents must increase the suspended solid content of the resulting domestic effluents which the sewage plant receives.

de Oude: If metals are carried through at present, they will still be carried through even when they are tied up with zeolite as they will be in an insoluble form.

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The rationale for a ban on detergent phosphate in the Great Lakes Basin

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Abstract Immediate reduction of phosphorus loadings to the Great Lakes is essential to slow accelerated eutrophication. The Great Lakes National Program Office of the US Environmental Protection Agency now advocates adoption of bans on detergent phosphates as the most practical and feasible means of immediately reducing the phosphorus loadings to the Great Lakes. This change in policy from previous reliance on removal by sewage treatment has been adopted for the following reasons:

(1) Bans on phosphates will reduce capital and operating costs of treatment and, where adopted, have met with consumer acceptance.

(2) In practice, treatment plants have not met design expectations for phosphate removal.

(3) Neither nitrilotriacetic acid nor other substitutes for phosphates have proved to be a public health problem.

(4) Reduction of phosphorus loadings to treatment plants avoids increasing levels of chlorides and total dissolved solids in effluents.

(5) Water quality has improved in small lakes with phosphorus reduction.

In summary, detergent phosphate bans alone will not reduce phosphorus loadings to the Great Lakes sufficiently for the long term but the Environmental Protection Agency has concluded that such action is necessary in addition to continued efforts to control non-point sources.

As Regional Administrator of one of the 10 regional offices of the US Environmental Protection Agency (EPA), the Federal agency with the chief regulatory responsibility for controlling air and water pollution in the USA, I want to take this opportunity to discuss why the EPA is concerned with the question of whether to ban the use of phosphates in cleaning detergents.

Region V, which covers the six states of Illinois, Indiana, Michigan, Minnesota, Ohio and Wisconsin, contains most of the Great Lakes Basin (see Fig. 1) (and is often called the Great Lakes Regional Office of the EPA). For this reason, the chief responsibility for policy matters concerning the Great Lakes

is lodged with the Regional Office rather than in Washington D.C. This responsibility includes participation in the work on the Great Lakes of the International Joint Commission, the bilateral agency established by Canada and the USA to deal with matters of mutual interest along the border between our countries.

The current revival of the debate over banning the use of phosphates in detergents was initiated by the Great Lakes Regional Office of the EPA. At present we are advocating such a ban only in the Great Lakes Basin. Although bills supporting such a ban have been introduced in both Houses of the Congress on the initiative of representatives from the Region, the Agency has been urging that such action be taken by the states rather than by the Federal government.

We have not taken such action without careful investigation and consider-

FIG. 1. US Environmental Protection Agency Region V.

ation, especially since it is a change from the general reliance on removal of phosphorus by sewage treatment that has prevailed for some years. Several factors have caused reconsideration:

(1) The role of phosphorus as the limiting nutrient for eutrophication in the Great Lakes has been confirmed.

(2) Phosphorus loadings have remained high and eutrophication has continued to accelerate in some locations in all the lakes.

(3) Experience with phosphate removal treatment has shown that design levels often are not achieved and treatment plants have not been constructed as rapidly as once was thought possible.

(4) Removal by chemical treatment not only is costly but increases the amount of sludge handling and discharge of total dissolved solids.

(5) A significant part of the phosphate loading, up to 20% in some places, results from atmospheric transport, but the means are not yet available for reducing this source.

(6) Practical and widespread means are not available for controlling runoff from the land or non-point source introduction of phosphorus into the Great Lakes.

(7) Experience with phosphate bans elsewhere has shown that non-phosphate detergents are accepted by consumers and have reduced the costs of sewage treatment. The reduced phosphorus loadings have been followed by less algal growth in certain waters.

(8) Banning phosphates from household detergents appears to be the means of immediately reducing phosphorus loadings at least cost.

The policy on phosphates has been reconsidered at the same time as the International Joint Commission has been re-examining water-quality objectives set by an Agreement between Canada and the USA in 1972. Within the Great Lakes Regional Office of the EPA, the policy was examined by a special committee on phosphorus, which I established about a year ago. In the remainder of this paper I shall discuss the findings of that committee and the reasons for its conclusion that phosphates should be banned from household detergents in the Great Lakes Basin.

Water quality of the Great Lakes, collectively the largest body of fresh water in the world, has been deteriorating since man began concentrating his activities on their shores. The 1972 amendments to the Federal Water Pollution Control Act (P.L. 92-500) recognized the special needs and importance of the Great Lakes by authorizing special research and demonstration programmes.

PHOSPHATES AS A GREAT LAKES PROBLEM

Also in 1972, the Great Lakes Water Quality Agreement between Canada and the USA was signed. The intent of this agreement is to restore and enhance the water quality of the Great Lakes system by adoption of common water-quality objectives. The Agreement established an effluent limit of phosphorus of 1 mg/l for all sewage-treatment plants that discharge more than 10^6 gallons (4.5×10^6 l) of effluent per day into Lakes Erie and Ontario, and the International Section of the St. Lawrence River. This limit is now being reviewed with other objectives of the Agreement.

One reason for the EPA's review of the phosphate bans was the fact that the International Joint Commission urged all jurisdictions in the Basin to adopt strict limits on the phosphate content of detergents to be used in the Great Lakes Region. This recommendation was based on the findings of the joint Water-Quality Board and other bodies of the International Joint Commission that eutrophication rates will continue to accelerate in the future in all lakes unless there is a drastic reduction in phosphorus loadings.

Nutrient enrichment of the Great Lakes occurs both from cultural point and non-point sources at specific shore locations and from the mouths of tributaries. Because dilution occurs further from the source, the impact of the phosphorus loadings varies with location and is most severe in bays and harbours. In Lake Superior, the Duluth-Superior Harbor exhibits definite signs of enrichment, as do other local areas on the southern shore, even though the largest Great Lake is considered to be the cleanest.

Lake Michigan has three areas with major problems: Green Bay, Milwaukee Harbor, and the Indiana Harbor and Ship Canal in the concentrated industrial and populated areas at the southern end. In Green Bay, total phosphorus effluents occasionally exceed the 1 mg/l limit in spite of substantial new facilities for the removal of phosphorus in the highly industrialized and populous Fox River Valley. Here, and near Milwaukee, the clear signs of advanced eutrophication in the Lake are associated with the large supplies of phosphorus received from the polluted tributaries.

On the US side of Lake Huron, a high concentration of nutrients, coliform bacteria and total dissolved solids is received from the Saginaw River system. This river contributes 30% of the total phosphorus loading to the Lake through Saginaw Bay, where total phosphorus concentrations of up to 0.058 mg/l have been recorded between 1965 and 1974.

The water quality of Lake Erie has received most attention from both the public and scientific investigators in the past decade, with good reason. In the open waters of Lake Erie, concentrations of chlorophyll *a* and total

phosphorus have increased. The increases observed in the western basin are believed to be due to increased resuspension of sediments. Overall phosphorus loadings have declined about 30% since the Water Quality Agreement went into effect, but the apparent reversal in the trend towards declining water quality in recent years is now believed to have been due to dilution with high levels of water in the Lake during the 1973–1975 period. Concern continues about the advanced eutrophication in Lake Erie.

Lake Ontario is the only Lake presently benefiting substantially from a ban on phosphorus detergents, and most indicators suggest relatively stable water quality from 1967 to 1975. Still, nuisance growths of the alga *Cladophora* are a problem, for which the most practical control is reduction of the input of nutrients, especially phosphorus. In this Lake, also, total phosphorus concentrations are highest near urban centres.

EUTROPHICATION AND ALGAL GROWTH

Eutrophication, as evidenced by heavy algal growths, received more attention from both scientists and the public throughout the 1960s. Control of eutrophication depends on the limiting-nutrient concept, which is derived from Leibig's *Law of the Minimum* that 'growth is limited by the substance that is present in minimal quantity in respect to the needs of the organism'. Although phosphorus is not the sole cause of eutrophication, it is the element required for plant growth which man can control most easily in the aquatic environment.

Phosphates enter waterways from several different sources. The human body excretes about 1 lb/yr (0.45 kg/yr) of phosphorus expressed as P. Current use of phosphate detergents and other domestic phosphates increases the *per capita* contribution to about 2.5–3 lb/yr (about 1.2–1.4 kg/yr) of phosphorus as P. The major phosphorus ingredient is soluble tripolyphosphate which is readily available for biological use.

In the Great Lakes, it is essential to reduce eutrophication rates as quickly as possible by reducing phosphorus loadings. With present technology, the only readily controllable source is sewage effluent, yet it has not been possible to depend on sewage treatment alone for two reasons. One is that some sewage-treatment plants have not attained consistently-reliable removal of phosphorus and the second is that, in other cases, the equipment for the removal of phosphorus cannot be installed where it is needed because of lack of funds or lack of a municipal sewerage system. Until means of controlling phosphorus from agricultural and urban run-off, atmospheric deposition, and anoxic regeneration from sediments are developed, reducing phosphate input

to sewage-treatment facilities by detergent phosphate bans is the most feasible step.

REDUCTION OF EFFLUENT LIMIT

In addition to urging strict limitations on detergent phosphates, the International Joint Commission is also considering whether the effluent limit should be lowered to, perhaps, as little as 0.1 mg/l for all municipal sewage-treatment plants. Mathematical models indicate that, even if the present 1 mg/l is ever achieved consistently at all possible places, there would have to be additional reduction of phosphorus loadings from non-point sources to slow the rate of eutrophication. Since sufficient control of non-point sources is not now possible, reduction of the effluent limit is being considered to lower loadings by presently available means.

SOURCE CONTROL

Some knowledge of means to control run-off from land has been gained through special demonstration programmes and studies under the 1972 Water Pollution Control Act, efforts will continue to obtain the cooperation of agricultural interests in using different methods of soil preparation and other measures to reduce run-off. The available phosphorus in run-off from 560 km^2 is comparable to that in the treated municipal waste from a town of 10 000 people. Nevertheless, control of non-point sources will require much more time, and reliance has been placed, meanwhile, on treatment with chemical precipitation in municipal facilities.

Unfortunately, in the Great Lakes most of the larger plants for treatment of waste water are not achieving the 1 mg/l limit (see Table 1).

TABLE 1

Number of municipal plants with capacities greater than 10^6 gal/d (4.5×10^6 l/d) reporting an average discharge of phosphorus of 1 mg/l or less

Lake	Number of plants achieving 1 mg/l limit
Superior and Huron	7 out of 57
Michigan	23 out of 77
Erie	38 out of 120
Ontario	11 out of 106

EXISTING BANS

Some locations in the Great Lakes have already adopted detergent phosphate bans as a way of limiting the use of phosphorus and its introduction to natural systems. Detergent phosphate bans are in effect in New York, Indiana, and the cities of Chicago, Illinois, and Akron (Ohio). Partial bans exist in Canada and Michigan. A total ban is under consideration in Michigan and Wisconsin and has been adopted in Minnesota, even though implementation has been delayed by a court challenge by the soap and detergent industry.

Decreases in phosphorus concentrations were measured in sewage within months of implementation of total bans. For one facility in Monroe County, New York, there was a 55% reduction between 1973 and 1975. From 1971 to 1975, Indiana noted average decreases from 12 to 4.5 mg/l, and the City of Chicago reports 40–60% reductions.

RATIONALE FOR DETERGENT PHOSPHATE BANS IN THE GREAT LAKES NOW

Excluding phosphates from detergents both conserves resources of phosphorus and reduces expenditure of energy and capital for treatment of waste-water. For plants using chemical precipitation the operating costs may be reduced by as much as 20%, or $0.80–1.20 *per capita* annually. The City of Chicago estimates savings of $55 million for construction alone as well as millions of dollars per year in operating costs. In both New York and Indiana, reductions of ambient levels of phosphorus and algal growth, that is, reduction in eutrophication, were reported within months of adoption of phosphate bans.

When national policy on phosphorus control was first being considered, one of the original barriers to the reformation of detergents in 1971 was doubt about the performance and safety of the substitutes then available. Progress has been made since then and available substitutes now include sodium carbonate, sodium silicate and citrate, as well as nitrilotriacetic acid (NTA). Other 'builders' are in various stages of testing and experiment.

In all locations where the phosphate ban has been adopted, consumers' initial doubts have faded away almost completely with experience. Not one housewife or organized consumer group appeared before the Indiana state legislature last year to support an attempted repeal of the Indiana ban.

In addition, concern about greater danger of poisoning of children by non-phosphate detergents has also proved unfounded in experience. The National Center for Poison Control Centers, a clearing-house for monitoring causes of accidental poisoning, has had only one death possibly due to inges-

tion of a non-phosphate detergent reported in the past few years. There is so little difference in morbidity from ingestion of phosphate and non-phosphate detergents that no distinction is made in keeping the records of poisoning from these causes in children. In 1975 less than 10% of children who ate or drank household detergents had symptoms of poisoning and even fewer were hospitalized, whether or not the substances contained phosphates.

We expect that, in any case, the soap and detergent industry itself will move to reduce the amount of phosphates in detergents within a few years. Nevertheless, the Great Lakes Office of the US Environmental Protection Agency has moved to urge banning of phosphates from detergents for use in the Great Lakes Basin as quickly as possible for all the reasons I have discussed. The reasons may be summed up by observing that protection of the quality of one-fifth of the world's supply of fresh water justifies urgent action, and we are trying to take it.

Discussion

Brydges: Your point about waste-treatment plants failing to remove phosphorus to the level of 1 mg/l is fair; probably none of the Ontario Ministry of Environment's plants achieves that level but such treatment does reduce the amount of soluble available phosphorus. We have instigated a major training programme for the operators of such plants.

Alexander: The tripolyphosphates, according to both our own and Canadian work, are readily available in the lakes whereas the other phosphates, from run-off, are not—maybe only 30–35% of run-off phosphate is available (Thomas 1976). That figure dramatically alters considerations about inputs to the lakes; for instance 65% of total phosphorus input into Lake Erie comes from land run-off. (That is not true for other lakes.) And 35% of that 65% is available to the algae in the lake.

Griffith: May I ask a question about the proposed US law? According to the Senate Bill (before Congress), I can add an adjunct that contains 20% phosphorus by weight to a detergent, provided that the adjunct is not in the detergent box. Does this mean that I can sell two boxes, the contents of which should be poured together into the washing machine, and stay within the law?

Alexander: That is not the intention of the Bill. However, the Bill provides that the EPA issues the regulations and I am sure that we can clarify the law!

Nielen: The biggest difference between our opinions rests in the question of what conclusions are drawn from results which may refer to different regions in different countries. Did I understand you to say that a phosphate ban will not reduce the eutrophic state of the lakes?

Alexander: I said that a ban will not solve the problem of phosphorus eutrophication in Lake Erie. We envisage that a ban of phosphates alone would ensure that Lake Superior did not deteriorate over the next 25 years (on present projections for growth). Lake Erie has the most problems, as it is the most shallow of the Lakes. Even though it has a rapid flushing time of 2.5 yr (compared with 100 yr for Lake Michigan), the state of the Lake (because of the controls that have been put on it) means that the phosphate ban by itself will improve the quality of the water but not solve the problem because of the other tremendous inputs to the lake. One of those other inputs is resuspension of the phosphorus already in the sediments—a major problem in Lake Erie. I cannot emphasize too much that what I have said refers only to the Great Lakes. Many other lakes in the USA are nitrogen-limited. For them a phosphate ban would not be desirable.

Nielen: That is most important because some governments in European countries may be influenced by the passing of a law in the USA to ban phosphates—even though the rationale for the ban may apply only to the Great Lakes. The conditions in Europe differ greatly from those in North America.

With regard to economies, the Swedes, who do not operate a phosphate ban, have not experienced such tremendous savings. Also, a recent study by the Battelle Institute (in Geneva) which compared the cost efficiency of phosphates and phosphate substitutes concluded that only small savings were possible by the reduced use of precipitating agents in the chemical treatment of effluents if phosphates were banned. I should add that all experts in Europe agree that chemical treatment is necessary in every case, whether there is a ban or regulation on phosphate or not. Western Europe cannot have the alternatives of phosphate or no phosphate; the latter would mean a substitute in detergents with no great saving in overall costs. Proposals have been put forward in the Netherlands to remedy the eutrophic state of the waterways by a ban on phosphate and the use of purely soap-based detergents, but the TNO Institute in Holland has calculated that the cost of sewage treatment would consequently increase by 20–30%.

I am surprised that the advanced sewage-treatment plants work so badly in the USA, especially so as such plants have been most successful, for example, in Sweden. Sweden has hardly any eutrophication problems. By January 1st 1976 more than 60% of the communities in Sweden with more than 200 inhabitants were connected to advanced sewage-treatment plants; that means that more than 650 sewage-treatment works had been built and were working with extremely good results.

Alexander: Are they removing phosphorus or do they just use secondary

treatment? I don't want you to misunderstand me to have said that our sewage-treatment plants are not doing what they were primarily built for.

Nielen: The plants I am talking about are designed to remove phosphate from sewage effluents.

Alexander: To what level? Very few of the plants around the Great Lakes meet the requirement of 1 mg/l—even though they may reduce the phosphorus concentration to 1.5 or 1.2 mg/l, for example.

Nielen: They remove phosphorus to concentrations of 1 mg/l and lower.

de Oude: The report of the Committee on Phosphates and Water of the German Chemical Society (1977) states that effluent concentrations of 1 mg P/l can be reached in sewage-treatment plants using aluminium or iron(III) salts. With iron(II) salts the effluent concentration can be lowered only to 2–3 mg/l.

R. J. P. Williams: Are these the results of a special test?

de Oude: No; they reflect current practice.

Nielen: Germany has 55 advanced sewage-treatment plants which service 2.5×10^6 population equivalents. These plants are designed for the removal of phosphorus.

Alexander: Phosphorus can be removed to the 1 mg/l level in such plants if the public is prepared to pay the price for skilled operators.

Nielen: In Sweden they can and they do.

Alexander: I have seen film evidence (from the soap and detergent industry) that it is not always true that there is no eutrophication in Sweden.

Nielen: I am quoting independent sources in Sweden (see Ulmgren 1973).

Collingwood: But, as Mr Alexander said, the costs are great; skilled personnel are needed to run the plants to get this removal consistently. Perhaps Sweden is prepared to pay for that but the USA is not.

Nielen: I am not saying that we have the solution and that no more research is needed. Of course in Sweden there are different situations from what happens in, say, Western Germany, Switzerland and the UK. But with regard to costs, the proportional cost for removing the phosphate coming from detergents is much lower than the overall cost of substitutes. According to independent limnologists, 10% of the population of the Federal Republic of Germany lives in catchment areas of lakes or slowly-flowing streams which are threatened by eutrophication. A statutory ban on phosphates would affect the whole country. One advantage of chemical treatment is that one can concentrate efforts to remove phosphorus in special local areas.

Alexander: I must reiterate that I am referring to the Great Lakes. They constitute 80% (by surface area; 90% by volume) of all the fresh water in North America (20% of the world's fresh-water supply, excluding the polar ice-caps)

and service 15% of the population of the USA and a major portion of the population of Canada—i.e. a limited area in which there is a serious problem. Research in one department of the EPA indicates that we would be foolish to consider a 1 mg/l standard *throughout* the USA.

de Oude: I understand that the data on phosphorus inputs in EPA Region V's Position Paper on a detergent phosphate ban (Region V Phosphate Committee 1977) are based on 1974 data (pp. 13–15 in that paper) and on 1975 data for the body of the report for Lake Huron and Lake Superior.

The phosphorus input data in the 1976 International Joint Commission Great Lakes Water Quality Board Annual Report (published July 1977), however, no longer support the key conclusions in the EPA's 1977 position paper. The phosphorus-loading targets can be met by municipal sewage treatment which reaches the 1 mg/l phosphorus effluent guideline, based on 1976 phosphorus loading data (see Table 1). Nearly all the plants in Canada are operating close to the 1 mg/l guideline. The phosphorus-loading targets in Lakes Erie and Michigan have not yet been attained because of the operation of six (out of more than 200) treatment plants. Thus, neither the Great Lakes Research Advisory Board recommendations nor those of the Great Lakes Water Quality Board to the International Joint Commission contain a recommendation to ban phosphates from detergents.

Alexander: That is untrue! It is true that the data in the book (International Joint Commission Upper Lakes Reference Group 1976) are 1975 data but the 1976 data (quoted in the Report I helped to write to the International Joint Commission in July 1977) continue to support the phosphate ban but show a tremendous improvement in the summer of 1975 in the anoxic condition of Lake Erie—only 4% of the hypolimnion was anoxic. We stated in the 1975 Report that we felt the reason for that was not improvement in the phosphorus inputs to the Lake but special weather conditions. This year's Report (1976) says that was true because the surveillance from last summer shows that the levels were back up to 60–70% anoxic in the central basin of Lake Erie. The 1976 Report (published in July 77) probably supports the ban even more strongly.

R. J. P. Williams: We must try to dissociate the scientific requirements in this issue from the political ones. Mr Alexander, you have had to make (very reasonably, if I may say so) a politically-biased statement. It is political in the sense that it is meeting urgent requests from people which are extremely hard to quantitate. We ought to be able to say on scientific grounds to what degree phosphate removal is a general requirement or a specific requirement for a particular area. Then we ought to be able to discuss the advantages of the two ways of removing the excessive phosphorus: treatment of sewage (with its

associated problems) and bans on the use of phosphorus.

Any body of water to which phosphorus is being supplied is idiosyncratic whether it is in the Lake District of the UK, a river, or one of the Great Lakes in the USA. The essential feature for that body is the maintenance of a steady-state that is consistent with its use. All we need to know, therefore, is how to maintain that steady-state; that is, to know the inputs and outputs of phosphorus and to control those quantities. Whether they are controlled by a ban on the use of detergent-builder phosphates or by treatment of sewage remains an economic or political question, unless some people maintain that, say, tripolyphosphate is the *only* detergent agent one can use for washing. If a suitable substitute can be found, tripolyphosphate will eventually be removed from the system and so alteration of the steady-state from this source will be prevented.

Pirie: You omitted another possibility, namely to take more things out of the water. For example, could all those fish in Lake Erie that nobody wants to eat be caught and used as animal feed? Similarly water weeds could be cultivated and harvested to remove some phosphorus.   .

Brydges: In Ontario, macrophytes have been removed from lakes to maintain the recreational purposes of those lakes (so that people can water-ski) but at the same time the Ministry of the Environment has studied the economic aspects of the operation. Unfortunately, harvesting is not an economic method of removing nutrients such as phosphorus. For trace contaminants such as heavy metals the estimated cost of removal is thousands of dollars per pound of contaminant removed.

Pirie: What did you use the weeds for afterwards?

Brydges: We used them as animal feed—we fattened 10 steers on it last year. Economically that was not worth-while because we had to supplement it with too many other food materials. Composting seems to be the most promising method of use, but I don't think it will ever be economic to collect the plants for their intrinsic value; we shall have to subsidize the harvesting for some other purpose, in this case recreation.

The alternative, which Professor Pirie mentioned, is removal of fish. But it is not realized that the value of fish on the market as food (whether for humans or for animals) is only perhaps a few dollars per pound (or down to a few cents per lb) but their value on the sport fish market (which is important for Canada) can be up to several hundreds of dollars per fish. So harvesting fish as food to remove phosphorus is not economic.

Pirie: But Lake Erie, for instance, has already converted itself into an eutrophic lake—the fish are there.

Brydges: That is true; but Lake Erie is not in the steady-state that we want

it to be in. This discussion echoes the debate in the 1960s about whether phosphorus removal would do any good, except then many papers were presented at conferences claiming that carbon was the limiting element. Although it may now seem obvious that phosphorus removal is a good thing, it was not accepted as such in 1970. The 1972 decision to ban phosphorus by Canada and some states in the USA put us out on a limb.

Alexander: Several studies are in hand on alternative methods of handling *Cladophora.* We have harvested *Cladophora* and used it as cattle feed but that was not successful—for a start, the cattle didn't like it. Another method which will take a long time to be accepted socially in the USA but which will alleviate much of the phosphorus problem is the treatment of sewage on the land, both by disposal of sludge on land and by treatment of the waste on land itself, in the growing of crops. In some large projects (e.g. in Michigan), the sewage never reaches the water; it is used as fertilizer and for irrigation of corn, for instance. This method is highly successful but it is not yet socially acceptable. For example, at a public hearing in Bemidji (Minnesota), a small town of about 12 000 people at the head waters of the Mississippi River with a couple of lakes down-stream that are limited by nitrogen not phosphorus, the town council wanted to use the sewage on the land because of the nitrogen-limitation problem but the inhabitants who lived near the land which was to be so used objected vigorously and obstructed the proposal, even though that is one of the best ways to treat sewage for phosphorus and nitrogen.

However, as Professor Williams said, this is really a simple issue and there are only a few areas of disagreement between the scientific community, government, the public and industry. Most people agree about what are the inputs of phosphorus to the Great Lakes. There is good agreement about what limits the Lakes can take (so far as being eutrophic or not is concerned). Two basic issues divide the soap and detergent industry from the government. (1) Are there substitutes available? The soap and detergent industry say that good substitutes are not available (even though their advertising suggests otherwise). (2) The soap and detergent industry in the USA accepts that there is a problem about phosphorus inputs to lakes and rivers but argues that the best way to remove phosphorus is by treatment of sewage rather than by a ban on phosphates in detergents.

R. J. P. Williams: This group cannot decide for or against sewage treatment as opposed to a ban on phosphate; as I said, that is a political question. We must first completely understand the inputs and the outputs to the region in question and also find out what the *use* of the body of water is. If the desirable steady-state use is limited by phosphorus we can define that and keep to it.

Griffith: Mr Alexander, did I understand you to say that the issue was

political and that a detergent ban would not do much to change the quality of Lake Erie?

Alexander: No, I said that politics enter into it; that for Lake Erie a phosphate ban by itself will not solve the problem in the long-term but will give some immediate improvement. In some of the Great Lakes the phosphate ban by itself will solve the problem for the next 25–35 years (as far as maintaining the levels that are needed in the lake). The big question is one of cost: is it more efficient to take phosphates out of detergents or to remove them to low levels at the treatment plant? That is the crux of the argument between the soap and detergent industry and the government.

R. J. P. Williams: It seems to me to be more complicated than that. I thought that in Sweden one way was held to be better but in the USA another way was accepted.

Alexander: Every lake or body of water is different. We have to determine the case for each lake; our Position Paper (Region V Phosphate Committee 1977) details this determination for each of the Great Lakes with evidence from many years of study.

R. J. P. Williams: Do you know what is the desirable steady-state as far as phosphate is concerned for each lake?

Alexander: We have the answer: the input of phosphorus to the Lakes must be reduced by so many tons per year (the amount is different for each lake). That conclusion is fairly well accepted. The question is how do we do that?

van Wazer: We all realize that the political aspect is important, but one feature of which I have become painfully aware is the attitude disseminated by the media to such phosphorus compounds as alkali metal phosphates. A common impression in much of the USA appears to be that phosphates used in detergents are poisonous in themselves (with no realization that the pollution problems stem from the life-giving qualities of these phosphates). This attitude results from distortions given by the media when 'phosphate pollution' was of general public interest.

Gilbert: Mr Alexander implied that he agreed that in the long run it will be necessary to have tertiary (chemical) treatment of sewage in the area of the Great Lakes. There has been some question about the extra cost of treating those effluents if they contain detergent phosphates. In some of the calculations done by the EPA it seems to have been assumed that this cost will be almost *pro rata* but this certainly has not been the experience in Sweden (Nilssen 1973) which suggests that both the cost of chemicals and the residual level of phosphorus after treatment are not by any means directly proportional to the incoming concentration of phosphorus. The Swedes, therefore, are convinced that once tertiary treatment plants are installed there is no need

for a phosphate ban the cost savings on chemicals and so on are relatively small.

Alexander: The costs of installing a tertiary treatment plant are not proportional to the phosphorus concentration in the influent (cf. costs quoted in the Position Paper); it costs almost as much to treat an influent containing 6 mg P/l as it does one with 10 mg P/l. The EPA has discovered that, if the phosphorus concentration in the influent can be restricted to 5 mg/l, tertiary treatment is not needed to lower it further to 1 mg/l; that can be done with secondary treatment with some chemical addition. The Swedish experiment overlooks the sizeable increase in sludge generation depending on the influent concentrations and, hence, problems with sludge disposal, which is expensive in the USA.

Gilbert: The conclusions in the Position Paper differ considerably from the Swedish conclusions.

McClellan: Just how expensive is an advanced water-treatment plant to operate?

Alexander: As an example, the plant in Ely, Minnesota, a town of 5000 people, costs $490 000 p.a. to operate to reduce the phosphorus concentration in the effluent to 0.035 mg/l. If the limit was eased to about 0.4 mg/l, which would still protect Lake Shagawa (which is part of the Boundary Water Canoe Area), the costs would be reduced to about $377 000 p.a. That works out at about $80 yr^{-1} per *person* that is an average $500 a year for sewage treatment for each family.

Reynolds: This issue will always be a matter of public and political attitudes. Although the gist of my message (pp. 201-216) may have sounded like 'don't worry about phosphorus', people will always worry about it when it is shown to cause obvious changes in the appearance of familiar lakes and rivers. Many lakes in the UK are already eutrophic and few people would notice if they became more eutrophic; they would notice when the fishing, water-skiing, swimming or whatever, was spoiled. But, as has become evident, we do have the ability to restore bodies of water or to maintain their steady-states (when we know what they are!) and so the problem resolves into one of how much is the public prepared to pay for them. That throws the issue back to the politicians.

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Can the availability of phosphorus be critical for mankind?

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Abstract The biological cycle of phosphorus differs from that of other bulk elements in so far that the complete cycle has a long half-life. The cycle is described and man's inputs are analysed. The immediate problems are the inputs to the environment of phosphate through fertilizers and detergents, but the long-term problem is the availability of workable sources of phosphate.

In presenting an over-view before the final discussion I want to draw attention to areas where our handling of phosphorus could be critical to the future of mankind. The scheme of reactions I shall use is shown in Fig. 1. It is the biological cycle for phosphorus. I shall point to the critical points in this cycle which we have mentioned earlier in the symposium. I start from the steps from rock to chemicals as these must be the sources of variation of the phosphorus input to soil or water whether this is by natural or man-made processes. We note the critical features: (i) the locality of the phosphorus ore on the earth's surface, (ii) the quality of the ore and (iii) the energy required in its handling. It would be foolish to suppose that there are no grievous problems here and that the known enormous deposits of phosphorus by themselves will save us from supply or financial problems when the political situation is tense. However, we have no scientific input into this problem. We can only show which areas are vulnerable through lack of phosphate, e.g. Europe, or which are vulnerable through over-population, e.g. India. I shall spend no further time with this type of problem and in what follows I shall assume that man can avoid political entanglements. In so far as phosphorus is concerned this is a local problem for the management of each country to consider. Let us suppose that this is done properly and effectively. This will mean that the phosphorus supply to life, i.e. to the 'available phosphorus' in Fig. 1, can be regulated up or down everywhere at will. Regulation on the
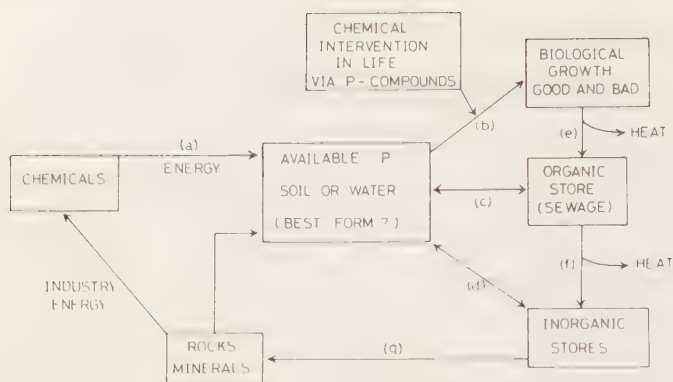
FIG. 1. A simple version of the phosphorus cycle of biological systems. The steps are described in the text. The nature of 'Available Phosphorus' is a matter for discussion.

down side includes legislation to limit phosphorus in detergents and to control sewage, and, on the up side, the need to increase the application of fertilizers (e.g. to the soil of India for the 'green revolution'). The problems which remain are largely controllable if proper advantage of scientific advice is taken, at least in the short term. In the long term we meet a critical situation of a different kind (see later). In whatever way the phosphate is applied (path *a* in Fig. 1), I shall assume that it is totally available to life initially. This means that the applied chemical forms of phosphate are readily available to biology at the moment of application. Obviously there is scope in the appropriate choices of phosphate chemicals in step *(a)* and even in their time of application. We need to know whether improvements in the fertilizers used at present and the methods of applying them are possible. In passing, I note that polyphosphate (in detergents) is an excellent fertilizer and is liberally added to water, albeit for washing.

The available P now controls the rate of growth *(b)* of valuable crops and of 'nuisance' life forms such as weeds, algal blooms *etc.* The rate of growth depends on the input of all chemicals, but phosphorus is one of major significance. Man has some differential control points over this growth since he can selectively interfere with life forms through drugs and herbicides, some of which are phosphorus-based. This area is not yet fully developed. We see that phosphorus supply is one major limiting factor on human population growth, since the continuation of life in any form depends on phosphorus being available, but this is not a control which we could use in an acceptable way. Thus we must think largely in terms of an increase in step *(a)* leading

selectively to an increase in *(b)* which should mean better living rather than more lives. We must hope that education will reduce population.

The continuation of growth *(b)* needs an input of energy, too, but this is supplied not by man but by the sun. Growth also produces waste *(e)*, sewage in the case of man, which is rich in phosphorus and can be returned to the available pool (path *c*). A more usual route to the organic store through path *e* is the decay of vegetation. Now for the first time we come to a small cycle within the large cycle: the processes *(b)*, *(e)* and *(c)* are partly cyclic. As such cycles are common in the consideration of the involvement of phosphorus in life we must consider them more carefully.

Let us assume no input at *(a)*, no leakage of available P to inorganic stores through *(d)* and no output from organic stores at *(f)*. Phosphorus is now trapped in a cycle and we are interested in the rates of transfer between three pools, assuming no losses. Process *(b)* is irreversible as is *(e)* virtually, and *(c)* is reversible in principle. The cycle must run in one direction and is energized by the sun. We see immediately that the size of the 'biological growth pool', its phosphorus content, is limited by the relative rates of *(b)*, *(e)* and *(c)*. In the limit of infinite time the pools each have a constant phosphorus content and the rate constants of *(b)*, *(e)* and *(c)* decide the sizes of the three pools. A slow decay of organophosphorus compounds *(c)* means (in the cycle) a large accumulation in the organic store pool and a small biological growth pool. We need to assist the transfer *(c)* from this pool if we want more food and healthier people. Can man do this since it appears that there is a large hold up of phosphate in the organic materials of the earth? (In contrast, sewage phosphate is probably cycled rapidly.) This is a worthwhile problem for study, involving soils in all types of terrain. Before passing to the other pathways, let us note that there are other similar cycles, through inorganic phosphate—for example *(b)* *(e)* *(f)* *(d)*.

The cycles so far described have been discussed as closed cycles but we know that this is not the case. Organic phosphate can decay to give not only available phosphate but also inorganic phosphate *(f)* which returns only partially to available phosphate *(d)*; much is lost to the deep earth, the ocean sediments *etc. (g)*. Thus the cycle is connected to an almost irreversible step, *(g)*, as the reformation of rocks which man can use is slow ($> 10^6$ years). The cycle *(b)* *(e)* *(c)* is connected to a loss path *(g)* and is no longer truly cyclic. This is the source of the long-term critical problem. We have two choices which will reduce the problem but they are not equally satisfactory. We can make up for the losses in *(g)* by increasing the amount of available P by *(a)*. If we do this we increase also the phosphorus which is held in the cycles. There is then more phosphorus in biological growth. Alternatively, we can try to reduce the

losses *(g)*. We can do this by manipulating the inorganic stores of phosphate so that inorganic phosphate returns from the store (soil) to available forms *(d)*. This may imply a change in our plants or lower life forms in the soil so that what is now called unavailable becomes available.

It would be the height of folly to ignore the dangers in the above problem. The total phosphate supply is large today but on the scale of life's existence ($> 10^8$ years) the phosphate supply rate *(a)* has a short half life of, say, about 100 years. The rate *(a)* is comparable with the rate of *(f)* but the rate *(g)* is very slow (10^6 years). Thus step *(a)* becomes the rate of dispersal of phosphate into unusable inorganic stores so that we cannot use it again quickly enough. The soil and seabed will become dilute phosphate stores and relatively soon. Absolute lowering of the amounts of phosphate in the cycles *(b) (e) (c)* and *(b) (e) (f) (d)* is inevitable in the long term. This means less growth of life forms and a lower density of *all* life forms on earth. The crux of the phosphate cycle is the slowness of the processes by which it can be made reavailable once it is dispersed in the soil or the sea.

Before looking at the ways out for man let us note that much, of the immediately available phosphate never enters the biological growth pool since phosphate added through *(a)* can be transformed directly, 'lost', through steps *(c) (f) (g)* or *(d) (g)*. Crops grow slowly. These steps could be better controlled by better biology and chemistry or better methods of applying phosphate perhaps. Note too, that phosphate and energy transfer in biology are comparable and that the phosphorus cycle differs from the carbon, hydrogen, nitrogen and oxygen cycles. There is little real loss of carbon, hydrogen, oxygen or nitrogen in their biological cycles since the rate of their equivalent step *(g)* is fast. Losses for nitrogen fertilizers are largely of energy. The energy steps are: fuel chemicals → non-fuel chemicals + heat, or light → heat. The phosphate step is: concentrated ore phosphate + energy → dispersed phosphate. Even within the phosphorus cycle energy *losses* (not cycles) are obvious ('heat' in Fig. 1).

Man can sustain life growth rates only if he increases *(a)*—using lower grade sources and more energy—or if he increases return steps *(c)* and *(d)* to available phosphorus or if he blocks off *(f)* and *(g)*. We should look at ways and means of achieving such ends now, especially in Europe, which has no significant phosphate ore of its own. If through political action difficulties come sooner rather than later, this can only make the need for research by chemists and biologists more urgent.

It may seem surprising but Fig. 1 is equally applicable to the other phosphate problems—the effects of detergent on ecology. The essential feature of all the problems is that a steady-state of available phosphorus, which is

consistent with the use to which the soil or water is to be put, must be maintained. This means that no change in life pattern can occur through the use of phosphorus, as phosphorus input equals phosphorus output. In a lake the major rate inputs of phosphorus, step *(a)*, are from chemicals, e.g. triphosphate (detergents) and rock, from sewage and other organic stores *(c)*, and from the lake bottom and the air *(d)*. Reversal of *(c)* and *(d)* removes phosphate as does the outward flow to the sea *(d)* *(g)*. It is immediately obvious that in this case *(a)* or *(c)* can be stopped. As much of the source of *(a)*, all the detergent, passes through the sewage works this is the point of control. Banning phosphates from detergents may be cheaper, politically easier and so on but is not an absolute control over phosphate input. It is essential to note, too, that the tolerable level of available phosphate is a unique quantity in a particular environment; it may even be good to let the phosphate concentration rise in some lakes.

A final remark is necessary on the 'reputation' of phosphate. We are bombarded today by references to pollution, and phosphate gets its fair share of comment. All this means is that the steady-state of phosphorus in some areas is now too high considering the use to which the land or water is to be put. The situation can usually be reversed rapidly (through the processes in Fig. 1). On the other hand, we do not read how phosphate has *enriched* our world since man increased the steady-state concentrations of available phosphorus over vast regions of the earth (i.e. the available P pool). As with all the other 'good things in life' the use of phosphorus remains overwhelmingly beneficial but excesses lead to undesirable consequences. I hope that in part this book will take the sting out of the phosphorus argument and lead to a much more rational discussion based on scientific appraisal before politics and economics take over.

Discussion

Larsen: First I want to support all that Professor Williams said. Secondly I want to elaborate one crucial point, namely the phosphate equilibria in soil. The number of studies on this subject is legion. They date back to 1845 when Daubeny (from Oxford) gave the Bakerian lecture at the Royal Society in London. In this lecture Daubeny distinguished between 'dormant' and 'active' ingredients of soil, that is phosphate and potassium, with reference to the plants that grow in it. He determined the active 'ingredients' by extracting the soil with water 'impregnated' with carbon dioxide and regarded this

fraction as being immediately available to the plants and the dormant in-gredients as being mobilized when the soil was allowed to rest (i.e. lying fallow). Using this concept Daubeny advocated that the fertility of soil with respect to P and K could be maintained by drawing on the huge reserves of these elements merely by choosing a suitable rotation of crops and fallow.

This type of soil management was not new but had been practised since the introduction of agriculture some 10 000 years ago. It goes under the name of shifting cultivation which even today occupies some 1×10^8 ha of the cultivated land of the world, particularly in South America, Central Africa, and Borneo (Indonesia) (Nye & Greenland 1960), and is a perfectly stable type of farming. The only snag is that it requires much land, as the soil has to lie fallow for some 20 years before the fertility has been restored and a couple of crops can be grown.

Be this as it may, a fuller understanding of the phosphate equilibria in soil was not gained until the advent of the radioactive phosphorus isotope ^{32}P some 30 years ago. With this isotope as an indicator for stable phosphorus, ^{31}P, the kinetics of the crucial process can be studied in detail and in chemi-cally-intact soil. This was first done by McAuliffe *et al.* (1948), who found that the process was rapid, with a half-time of a few minutes. This has since been confirmed by numerous other researchers. Furthermore, the use of ^{32}P makes it possible to calculate the amount of soil P which takes part in the exchange of phosphate between the solid and liquid phases in soil. That amount of soil phosphate is termed isotopically exchangeable phosphorus (the E-value) (Russell *et al.* 1954; Russell 1957).

$$P_{soil} \rightleftharpoons P_{soil\ solution}$$

If the truly active phosphorus of a soil is to be determined with reference to the plants that grow in it, ^{32}P must be introduced to a soil plant system and the amount of isotopically-dilutable soil phosphate determined on the basis of the $^{32}P/^{31}P$ ratio in the plant (Larsen 1952). The amount of active or labile phosphorus in the soil determined in this way is not identical to the E-value and it is, therefore, termed the L value (Russell *et al.* 1954) (see p. 195). It represents the phosphorus which takes part in the supply of the plants with phosphorus. This is a comparatively small fraction, e.g. $2–10 \times 10^{-5}$ of the total P in the soil (i.e. $4–12 \times 10^{-4}$ of the P in the soil). The bulk of the soil phosphorus is thus non-labile or, more correctly, dormant as Daubeny would have said.

Between the labile and non-labile soil phosphorus there is a slow but reversible process;

$$P_{non-labile} \rightleftharpoons P_{labile}$$
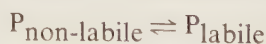
The half-time of the movement of P from labile to non-labile has been estimated (Larsen *et al.* 1965): it varies between 2 and 6 years in mineral soil. The velocity of the reverse process has still to be estimated but it may be assumed to be of the same order of magnitude as the opposite process. That this process in fact occurs is evidenced by the successful practice of shifting cultivation and long-term experiments with plots to which no phosphorus was applied.
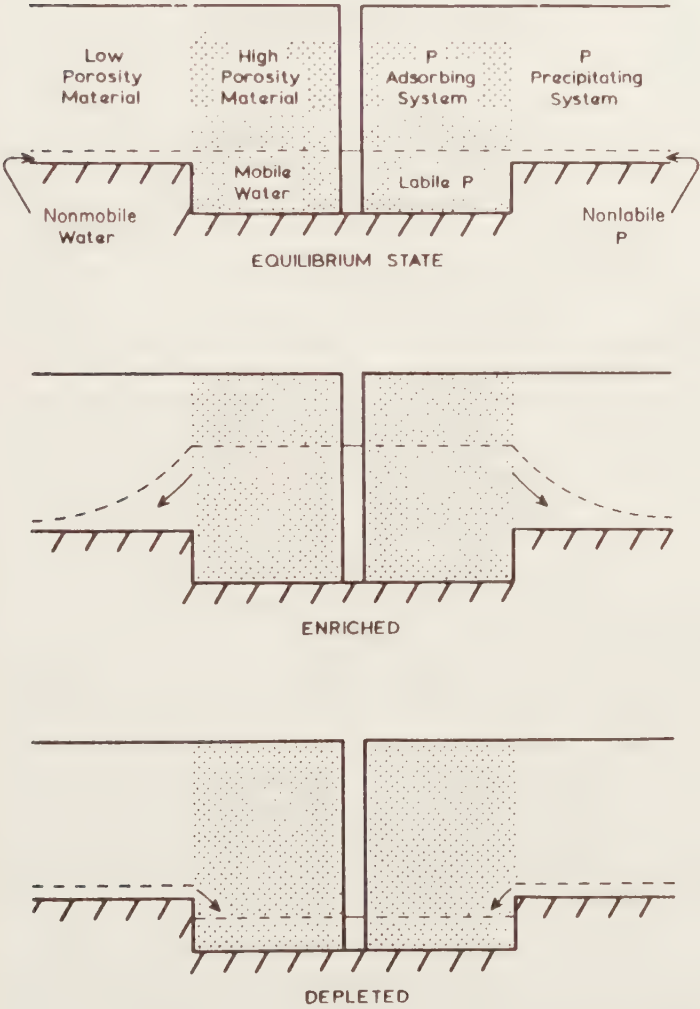
Fig. 1   (Larsen). Well analogy. depicting the behaviour of phosphorus in soil (Larsen 1967).
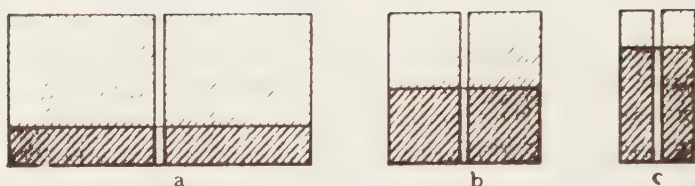
FIG. 2 (Larsen). Capacity of system to retain phosphorus (= water, in the well analogy). The same amount of phosphorus (heavy shading) is held in 'wells' of different sizes with different sorption capacities (from Sutton & Gunary 1969).

The system described can more vividly be depicted by considering the analogy of a well (Fig. 1). This analogy also illustrates the lesson taught by Schofield (1955), namely that a plant must expend work in order to draw phosphate from the soil—the work that must be done to get water up from the well. It also shows the close relationship between the amount of labile P and the work required to draw phosphate out of the soil (water out of the well).

Likewise the importance of the system's capacity to retain phosphorus (or water) is obvious from Fig. 2 in which the sum quantity of water (= labile P) is shown in wells (= soils) with different sorption capacities.

The schematic presentation of phosphate equilibria in soil (Fig. 3) may serve as a conclusion of my rather long point.

This is the system we want to manipulate. But how? First we must stop or slow down the formation of the fractions C and D (Fig. 3). This is easier said
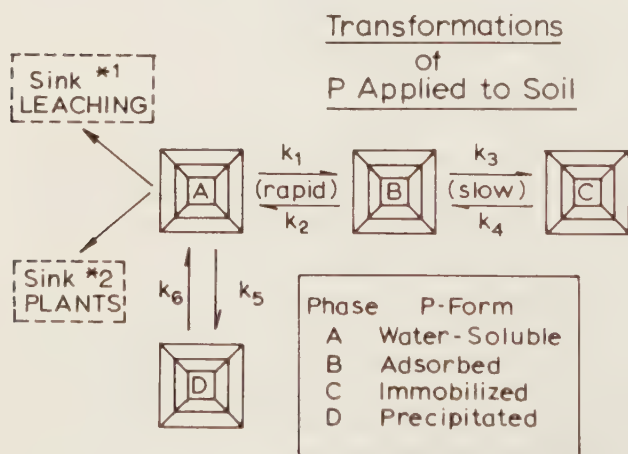
FIG. 3 (Larsen). A schematic representation of six reversible kinetic reactions which are assumed to control the transfer of applied phosphorus between solution, adsorbed, immobilized (chemisorbed), and precipitated phases within the soil. Sinks are shown for irreversible removal of phosphorus from the soil solution by plant uptake and by leaching (from Mansell et al. 1977).

than done but we must start somewhere. Thus one can impede the formation of crystalline phosphate by introducing an agent which will 'poison' the nuclei. Such an agent is diphosphate ($P_2O_7^{4-}$); it impedes the growth of calcium phosphate crystals. It is used for this purpose in toothpaste and its effect on the formation of calcium phosphates in living organisms has been studied in great detail by H. Fleisch and his co-workers in Lausanne.

Diphosphate prevented formation of crystalline calcium phosphate when di- and mono-ammonium phosphates were added to a calcareous soil (Larsen & Widdowson 1966). Diphosphate is, however, unstable in soil (Sutton *et al.* 1965). A more-lasting effect may be obtained from diphosphonates, which contain a P–C–P bond instead of the P–O–P bond of diphosphate; Francis (1969) showed that diphosphonate prevents formation and growth of insoluble calcium phosphates. It would be tempting to test diphosphonate as an inhibitor of phosphate precipitation in soil.

Tinker: Professor Williams, I too support all that you said and I was delighted to hear you encourage us to do more work on the soil→plant movement (even though I have been working flat out on it for five years!). You put your finger on the question of the store of P and available P and how one can get more into plants. This problem is a priority for research. I will take you up on one point only; you said that this is the place that chemists have to do something about. That is only true in part because chemists alone will not solve it. Perhaps one reason why the work is not further forward is because of insufficient collaboration between plant physiologists, biologists and chemists in the past.

Griffith: Professor Williams, you used P to denote elemental phosphorus but we have hardly mentioned elemental phosphorus, inorganic metaphosphate, ultraphosphate, P_2S_5 or any of the chemistry of such compounds, mostly made from elemental phosphorus. But then little research is being done in this area. The decline of the elemental-phosphorus industry which funded that research has seen to that. This decline brings in its wake much hardship to those communities which grew up around the industry. For instance, legislation outlawing the use of phosphates in detergents could turn Columbia, a town in Tennessee of some 30 000 people in which Monsanto is a major employer, into a ghost town. Obviously I am more concerned about those 30 000 people than about a limit of 20 μg P/l or whatever in Lake Erie.

R. J. P. Williams: That issue with its direct political overtones can only be settled between the industry and representatives of government in local regions. It is not a problem for scientific analysis. Similar problems arise in many industries elsewhere.

Griffith: It's not just a national problem. Any US decision will have repercussions throughout the industry globally. [See also p. 277.]

Brydges: To return to Professor Williams' diagram, I should point out that the pathway from 'available P' through 'growth' to 'store' (and from stores to and from available P) for soil differs greatly from that pathway in the aquatic environment. In many respects the problem with that cycle in North America is sociological: whether people want to and are prepared to change their thinking. For years people have been trying to stop that cycle because its only consequences seem to have been bad—algal growth, dead lakes etc. But that is not necessarily true. Other areas of the world where aquaculture has been practised for thousands of years are far advanced in the practice of returning stores of P to available P by harvesting weeds and a whole battery of other techniques. The problem in Canada is persuading people of both the need and the desirability of producing significant amounts of protein and that this can be done with a good use of phosphates in the aquatic environment.

R. J. P. Williams: That means introducing more phosphorus into the water in some places rather than less.

Brydges: Yes. For soil you identified a fundamental research need—investigation of the path from stored P to available P—but that same need does not exist in the aquatic route. We know how to get phosphorus back; it can be recycled. Our attitudes to the consequences of growth regulate our manipulation of the cycles.

Reynolds: I entirely agree. Although we can supply rate constants and other data for the various steps in that diagram we cannot quantify the emotive element of what is good and what is bad.

McClellan: I cannot agree with your statement that little or nothing remains to be done on the chemical side of your diagram. If we look beyond the limit of the UK and other countries with temperate soils, we can do a great deal to increase the efficiency with which phosphate fertilizers are used. I won't pretend that such advances will necessarily come from plant genetics or anything like that but I shall give one simple specific example. In certain so called 'high-fixing' soils (whatever that means) silicates can be used to change the proportion of phosphate which is classified as 'inert'—the fixation of silica on some soils can be diminished by prior treatment or co-treatment with other anions. We may be able to change the nature of the 'store' by improved technology. It would be short-sighted to assume that the fertilizer industry has done everything that it can to make these materials as efficient as they perhaps can be.

R. J. P. Williams: Silicophosphorus compounds can be made. Recently, Weiss (1978) in Germany found one such compound in the lungs of patients

suffering from asbestosis. Possibly some Si O–P compounds will release phosphorus in a controlled way.

McClellan: 500 000 tons of silicophosphates are prepared each year in plants in Brazil, Japan, Korea, China and South Africa. They have been used in agriculture for more than 40 yr and are still being used. Silicophosphates are reasonably well known; they are combinations of crystalline compounds and glasses, usually prepared by thermal processes. They have two major disadvantages: (1) they are usually low grade and (2) they need a great deal of energy to prepare. However, for certain types of crops they are particularly advantageous: coffee, tea, coconut, rubber.

There is more to the uses of silicates than the two or three topics we have touched on but I didn't want to limit our discussion to the chemistry of fertilizers (including metaphosphates and polyphosphates). These include phosphates with low solubility in water (controlled release) and associated trace elements and liming effects. This is one of the main uses of basic slag.

Larsen: We may be talking at cross-purposes. The interaction of silica and phosphate has been known for a long time. As Dr Harrison mentioned in his paper, the capacity for soil to adsorb phosphate on the surface varies widely. If this capacity is large, a lot of phosphate has to be added to bring it up to a certain level (see Fig. 2). One can manipulate that with silicate which competes with phosphate ions for the absorption sites on clay minerals (or other aluminium surfaces). Thus the phosphate adsorption capacity of the soil can be reduced and the phosphate is more readily taken up by the plants.

R. J. P. Williams: These silicophosphates (Weiss 1978) contain a Si—O—P group analogous to the P—O—P of pyrophosphate.

McClellan: That material is known as nagelschmidtite (see Table 4, p. 61).

R. J. P. Williams: Si is not the only substitute for P in the P—O—P linkage: boron gives a series of B—O—P compounds. But these Si compounds, as Dr McClellan said, are prepared by high-energy processes; in general, it is hard to make silicophosphoanhydrides by dehydration. The compounds found in lungs (with about one phosphorus atom for every six or seven silicon atoms) must be made by a low-temperature, low-energy process and they are not known as minerals. Silicosis is a major medical problem and discovery of these compounds could be a significant step forward in the recognition of a causative agent.

McClellan: There is an isomorphous series with silicocarnotite at one end and nagelschmidtite at the other and a continuously variable composition in between; it could be any one of those compounds.

R. J. P. Williams: Weiss checked the literature thoroughly and claimed that this Si—O—P compound has not been previously identified.

Arthur: Much experience has accumulated about the use of silico-phosphates. The steel industry, a high-energy industry, discharges phosphatic slags, which have been used effectively as fertilizers for many years. But there is no evidence that the efficiency of use of phosphorus from them is markedly higher than it is from orthophosphate. Silicocarnotite and nagelschmidtite are components of these slags.

McClellan: The main components of slags are wollastonite ($CaSiO_3$) and galenite, the high alumina equivalent compound.

Larsen: When the amount of available silicate in the soil increases, more gets into the plant where it has a significant effect on several serious diseases in rice; it protects the plant to a considerable extent. (That is why the Japanese use silicates.) It stiffens the straw and, when deposited on the leaf surface, it protects against leaf diseases (e.g. rice blast).

McClellan: Some plants have a requirement for silica, but many plants have a requirement also for magnesium which is used in the preparation of many materials. A lot of magnesium silicophosphate is used on tea plants, partly as a good source of magnesium.

R. J. P. Williams: I take the comment to be that we may possibly be able to improve our knowledge about the conversion of chemical P into 'available' P. When we know the chemistry of P—O—X systems, which must be a relatively easy task, we need not put more effort into that part of the diagram (i.e. the initial input of phosphorus to soil).

Shaw: May I return to the 'growth' part of the diagram? I should like to reverse the arrow from growth to sewage, as sewage can be a source of nutrients. I also take issue with the statement that, even if the world population remains constant, we shall not need any more fertilizers; three quarters of the world population need to raise their standard of living to a decent level and this process will need a vastly increased output of food.

Two fates awaits PO_4 fertilizers after application: either the phosphate is available to plants or it is not so readily available to plants. For a given fertilizer we can alter its marketability in three ways: we can change the handling costs (e.g. its transport); we can change the production costs; and we can change the quality and yield of crops grown with it. How much scientific and economic effort should be devoted to trying to find out the proportion of phosphate from fertilizer that is available to plants and the proportion that is not readily available to plants? If a new fertilizer is developed, can we put figures on the relative handling and production costs and the benefits in terms of quality and yield of crop? How much effort should we spend trying to do this? Also, what are the relative contributions to the bank of available P from freshly applied chemical fertilizer phosphorus and from the stores of

phosphorus already present on the soil? Furthermore how much effort should we put into improving each route?

Loughman: One intractable problem is the loss of a certain amount of the phosphate from fertilizers to the store by adsorption. Do we need a form of phosphorus that can be put onto the soil and not be broken down and adsorbed but will be taken up and metabolized by the plant? The low-bulk P–N compounds (see e.g. p. 169) may be suitable; they might by-pass this wasteful absorption process in the soil. (Obviously when the plant dies some of the phosphate goes into the store.)

McClellan: An even simpler approach is foliar application or hydro-ponics—the fertilizer does not have to pass through the soil.

Arthur: Farmers are stuck with soil! The answer to Dr Loughman's question is yes, but what is the ideal phosphorus carrier? What confounds research on this is the affinity of phosphorus for oxygen. A promising material will probably be intercepted by water in the soil and hydrolysed to orthophosphate so raising again the original problem.

One cannot speak specifically enough to identify the costs about which Professor Shaw asked but, as I tried to emphasize, the logistics of fertilizer manufacture are important from the economic aspect of using phosphorus. The value of a compact, concentrated fertilizer depends on where it is made in relation to where the phosphorus occurs naturally; for instance, manufacture at the mine saves the cost of transport of the ore. Another factor implicit in his question is the advantages that large manufacturing plants confer and the capacity effect—how much can be saved in unit cost by enlarging a plant? Too great a size, such as in single-stream plants, can be most disadvantageous if the plant breaks down.

McClellan: The nitrogen-fertilizer industry is much concerned about trying to make a product with controlled solubility or controlled release—materials which have either controlled chemical solubilities or some physical barriers applied to them such as a coating. I am not suggesting that we make coated fertilizers but that the concept that the uptake of nitrogen fertilizer be matched to the uptake by the plant might not be as unrealistic now as it was at one time. Water-soluble phosphates were developed as a result of fertilizer control laws—a political decision which made a considerable impact on fertilizer technology by changing the nature of the product. The resulting present-day products may not necessarily be the best compounds but they will be around for some time because of the money invested in plants to produce these products.

J. H. Williams: We shall probably depend much more on water-soluble phosphate in the future, because the production of the type of basic slag that is

worth grinding has dropped, owing to the change in the steel-making process (which now produces slags with only about 3% P_2O_5). From 1970/71 to 1974/75 the production of basic slag dropped from over 100 000 t (100 kt) P_2O_5 down to 30 kt and over the same period there was an overall drop from 500 to 400 kt of total P_2O_5 applied. This is unfortunate, particularly for acid soils which are known to adsorb phosphate firmly, because this material gave increases in crop yield which were better or as good as those from water-soluble phosphate both in the year of application and one or two years subsequently, at least in crops not particularly responsive to phosphorus such as grass or cereals.

Tinker: We are in danger of becoming unhealthily optimistic about new fertilizers. Three points have arisen. First, new phosphorus fertilizers may be made that are not adsorbed and are not lost in the soil 'store' of P. But we should be clear what remarkable properties we are asking from these compounds: they must not be adsorbed on all the different adsorbent surfaces in the soil; they must be resistant to a host of enzymes; at the same time they must be free to be taken up by the plant. Resistance to soil enzymes presents a problem because the plant has to hydrolyse the compound to orthophosphate—they must be enzymically hydrolysable in some way. However, let us assume that a compound has been made with the right adsorption properties; it is held in soil so hard that it is not leached away but not so hard that it cannot be removed easily. Remember that nitrate, for example, which is the least adsorbed of all the ions, is rarely used with better than 50% efficiency (in nitrogen fertilizers) even in optimal circumstances. So a phosphate fertilizer, even with these remarkable properties, will not be used to 100% efficiency.

The second idea was blockage of the adsorption sites in the soil with continued use of orthophosphate in fertilizers. I am sure that technically this is possible. The competitive adsorption of many different anions (e.g. fluoride, strongly adsorbed) has been reported. But before we get excited about silicates let us remember that about 90% of the weight of all soils is silicate and that the average soil solution contains about 1 part in 10^6 of polymeric silicic acid (which, incidentally, is taken up by plants where it forms phytoliths). So there is plenty of silicic acid in the soil already. The silica story started in the 1840s and at Rothamsted some plots of ground still receive silicate because Lawes thought that such treatment was a good idea. But evidence is lacking that silicate does any good over a long time.

McClellan: On the contrary: it is extremely effective on tropical soils, rich in aluminium but with very low concentrations of silica. As I mentioned, unfortunately the scope of our discussion has been limited to temperate

climates and largely to the UK and that is not where the world phosphorus problem exists! The only large areas of potentially arable land not presently in use are in Brazil and Sudan. These areas have tropical soils, climate, and crops. Our present 'temperate-zone' technology may not be optimal for such areas where conditions differ greatly. I suggest that, as our knowledge of these areas increases, we can better judge the similarities and differences in requirements. At present we cannot make this judgement because of a lack of information.

R. J. P. Williams: I realize that the scheme in my diagram refers to a particular locality and, for that reason, it is most important that we should qualify our statements with respect to the particular region in question and not generalize for all regions (or biological species).

Tinker: Some soil scientists have spent a long time working on Nipe clay in Cuba which contains 70–80% of sesquioxides and is not a typical soil. If anything, the most usual tropical soil is ferralitic. That does not mean that it is composed of sesquioxides—the usual soils contain large quantities of quartz with fine coverings of iron oxide.

McClellan: I don't disagree; I am saying that the possibility of controlled release or competitive anionic reactions is not beyond our technical scope in the production of fertilizers. In the instance I was referring to, steel slag from Germany was used on coffee plants in one area in the southern part of Brazil to demonstrate that soluble silica could be used to suppress the adsorption of aluminium at that site. That was one isolated experiment and illustrates that, although we know what the principal problems of fixation are, we should not discontinue working on them.

Tinker: Many effective competitive adsorbers are organic anions—citrate, malate and so on—but many of them, or their analogues, are present in the soil all the time. In effect we are dealing with situations in natural soils where there is already competitive adsorption; the soil contains many good competitors already. I am not saying that synthetic competitors cannot be made but warning that it is not a simple thing. A material is needed that is much better than the natural competitors. Finally let us not forget that a 15-cm-deep layer of soil contains about 2000 t/ha; the compound must be cheap for treatment of that amount of soil.

The third point to be raised was the method of application. Foliar application certainly is more efficient but one trouble with that method is that the plant must have enough leaf to catch all the spray before it can absorb it. Placement has not yet been mentioned—the use of ordinary soluble superphosphate in such a way that it can saturate strongly a small fraction only of the total soil volume.

McClellan: None of the reported studies on placement comes to any startling conclusions but your points are well taken—some basic issues in this area need some additional work.

J. H. Williams: The advantage of placement (more so for cereals and potatoes than for other crops) is noted most on soils that are very deficient in soluble phosphate. Once the phosphate status has been raised (as has already happened for most arable soils in the UK) placement does not bring the same benefit (at least for cereals). Potatoes, which respond well to phosphate, still benefit from broadcasting the fertilizer over the ridges (a form of placement) or placing it in bands to the side of or below the planted tuber.

Loughman: Taking placement to its logical conclusion, perhaps one should mention special cases such as rice which is transplanted or horticultural conditions in which Brassicas are grown. The young plant can be grown in a seed bed packed with phosphate for three weeks before being transplanted into a soil with a high binding capacity for phosphate but with little available phosphate. After the luxury feeding, the plants' vacuoles are full of phosphate. Once the crop has grown to a canopy, further phosphate (if needed) can be added by foliar feeding. That overcomes the difficulty of interception.

Larsen: I agree that placement is valuable in the early stages of crop growth, mainly because it reduces the amount of soil able to adsorb the phosphate and gives a high local concentration of available phosphate with a 'starter' effect.

Rice was mentioned. There are two kinds of rice: upland rice, which is rain-fed and responds well to phosphate, and paddy rice, which does not respond because in the anaerobic conditions that pertain in paddy soils phosphate is mobilized since the iron(III) is reduced to iron(II).

Foliar application has its advantages but only plants with plenty of phosphate have good foliage and the starving plants do not get the phosphate they need. Furthermore, as phosphorus is extremely mobile inside the plant, as has been shown by Hevesy *et al.* (1937) using ^{32}P, the plant will actually excrete phosphate after its aerial parts have been loaded with it.

I don't go along with the optimistic view that phosphate supply is not a problem: in many parts of the world, such as Australia, it is a problem (as we heard, p. 72) in spite of the newly discovered deposits in Queensland.

Griffith: Elemental phosphorus was once suggested as a fertilizer. That may sound a ridiculous idea, but when it was tried the results were surprisingly good (Monsanto Co., unpublished results). Red P gave better results than white P.

Larsen: Red phosphorus has been tried as a fertilizer in New Zealand

(Rothbaum *et al.* 1965). Even phosphine has been used (Hunter & Thornton 1956), mixed with anhydrous ammonia. (It was immediately oxidized to orthophosphate.)

Griffith: Will phosphite work as a fertilizer?

Larsen: Yes, it works well providing it is allowed to be oxidized to orthophosphate. Red phosphorus is oxidized too slowly and, therefore, needs a metal such as a copper salt to catalyse the oxidation to phosphate.

R. J. P. Williams: Phosphorus is not oxidized directly to phosphate. It goes to hypophosphite first.

Larsen: The soil was treated before the crop was planted so that, at planting, only orthophosphate was there. No toxic effect was observed.

SEWAGE TREATMENT

R. J. P. Williams: In sewage works does the phosphorus escape the primary treatment by living organisms because the nitrogen–phosphorus balance is disturbed or because some other element is in short supply, or what?

Collingwood: The consumption of phosphorus is limited by a shortage of carbon and nitrogen. The C:N:P ratio in sewage is about 30:7:1 whereas in a bacterial cell it is about 50:15:1. In other words one would need to double the carbon and nitrogen content of sewage to make its content comparable with that of a bacterial cell and that makes no allowance for cell respiration. Jenkins & Menar (1967) examined the kinetics of phosphorus assimilation in the activated-sludge process and concluded that the maximum removal of phosphorus by biological processes could not exceed 20%.

R. J. P. Williams: So addition of carbon compounds in the primary treatment should remove the excessive phosphorus.

Collingwood: Yes; one could then harvest it in the sludge. But carbon is expensive: methanol, a relatively cheap source of carbon, costs £80/t.

van Wazer: CO_2 is not expensive but the time and volume of gas needed for treatment bring in hidden costs. Suitably-rapid growth of organisms which obtain carbon from the air by photosynthesis needs large volumes of CO_2.

Tinker: Is it a more expensive process than adding aluminium and iron salts and subsequently collecting the phosphate?

R. J. P. Williams: Precipitation of aluminium or iron phosphate is an effective short-term economic solution but gives a useless product. If the phosphate can be taken up by organic compounds, it can be returned to the land; that would be far more worthwhile than building sewage plants which produce useless material.

Pirie: Surely if one wants to conserve carbon one should not aerate

sewage? There is no sense in removing carbon by aeration only to add it back to conserve phosphorus.

Collingwood: The prime aim of sewage processes is to remove carbon, a serious pollutant, as cheaply as possible. The best way to do this is by oxidation; even if sewage were anaerobically digested carbon would be lost as methane.

de Oude: Several pieces of research suggest that better long-term solutions are feasible. The biological removal of phosphorus by the mechanism of luxury uptake initially attracted attention but still is too difficult to control in the practical conditions in sewage-treatment plants. Other workers (Levin *et al.* 1975) have applied recycling of algae to make major reductions in the use of chemicals. Such as yet unconnected pieces of work suggest that much remains to be done and imply that in the future a reduction in or elimination of the use of chemicals can be achieved.

McClellan: Molecular flotation is also used to treat tail waters but, although successful, it is expensive at present. Various other chemical treatments include ionic flotation, electrical separation, and microfilters. Some of these methods show excellent results particularly for removing heavy metals as well as phosphates.

TRIPOLYPHOSPHATES

R. J. P. Williams: Let us now turn our attention again to tripolyphosphates. Mr. Alexander, by virtue of his position, presented a more or less political case for banning phosphates from the Great Lakes area, and it was necessary for all of us to hear that statement. The scientific basis of the statement is contained in the Region V Phosphate Committee's Position Paper (1977) [which was available to all the symposiasts].

de Oude: It is desirable for this discussion that the basic concepts are clearly defined. There are three variables: the *inputs* of phosphorus into a body of water, the phosphorus *concentration* (which determines the algal growth, assuming that all other nutrients are available in sufficient amounts) and the *quality* of the water. Historically, the words eutrophic, mesotrophic and oligotrophic are used as indicators of the water quality, but they should not be used in this way. The terms that can be used to describe the quality of the water are, for example, Secchi-disc depth, chlorophyll *a* content, amount of dissolved oxygen, and primary production.

The authority responsible for a body of water (a lake or a reservoir) must first specify the desired water quality. This quality depends on the concentration of phosphorus but this variable is not a suitable tool for water

management. Models exist that relate water quality to the phosphorus concentration but they include parameters such as the amount of phosphorus available from the sediments and require a quantitative description of the processes occurring at the sediment–water interface.

The practical difficulty of quantifying such parameters has resulted in models that immediately link the phosphorus loading of a body of water to its quality. The loading depends on the concentration of phosphorus in the input, the flow rate of the input streams, the surface area of the lake, the lake depth and the residence time of the water in the lake.

A given water quality specifies in these models the permissible loading and the water manager can select which factor is accessible to change in order to reach the desired loading. Frequently, the factor to be changed is the concentration of phosphorus in the input, but in some cases the total flow can be changed. One way to do this is flow diversion. It may mean passing the problem down-stream but it can be a valid solution for reservoirs.

The other factors—surface area, depth and residence time—are not so accessible, although cases are known where the depth has been changed (Anon 1974).

In conclusion: first define the objectives, then decide what to do.

Alexander: I agree completely. I must re-emphasize that every lake is different; the quality that is desirable for a specific purpose on the one lake may be no good for another lake. For example, in Texas many lakes support catfish but the quality of water for that purpose is entirely different from the quality of water needed for trout to grow. The data in the Position Paper are based on the quality that the people, through their laws, States and so forth, have decided that they want. Dr Griffith (p. 293) mentioned unemployment as a consequence of laws being passed but in environmental issues in the USA we have continual argument about the effects of any environmental requirement, especially on employment. Compliance with certain environmental requirements causes unemployment in some areas but usually it is more than offset by increased employment somewhere else; of course, that is no answer for the individual who loses a job. Underlying all our discussions is the fact that, even though there is a scientific basis, most final decisions on all these matters are political.

Griffith: The scientific basis is not a definitive scientific base. For this reason the final decisions are political rather than scientific. The main thing in approaching this subject is the different types of lake modelling: whether or not we can predict, in open waters, the influence of phosphorus inputs into lake waters. We could talk a bit about the Beer's Law approach to nephelometry and about how far a man with good eyesight can see a black-and-

white disc (the Secchi disc) on the end of a rod as the type of scientific basis on which decisions cannot be made.

R. J. P. Williams: The various possible replacements for phosphorus in the detergent require a difficult piece of scientific investigation but the subsequent selection of one in particular is not made on a scientific basis alone; external pressures usually settle the issue (e.g. economic and/or presumed or known biological effects).

McClellan: We have been told about the mobilization of heavy metals by polyphosphates which might be derived from detergents. Can these polyphosphates persist at the pHs that exist in treated water for any length of time?

van Wazer: Degradation in tap water from a purification process using chlorine or peroxide is slow and depends on the pH. In rainwater or river water, however, as long as the pH does not kill the organisms, the polyphosphates are degraded in an hour or so.

Johnston: Investigations at the Oxford sewage-treatment works (Perry *et al.* 1975) have shown that the bulk of the condensed phosphates used in household detergents are hydrolysed to orthophosphate before reaching the treatment plant, and the small quantities which remain are hydrolysed during passage through the sewage works. It is, perhaps, worth mentioning that in the UK the Secretary of State for the Environment is advised on all matters relating to the effects of surfactants and related products on sewage treatment, natural water and water supply, by the Standing Technical Committee on Synthetic Detergents. This committee was appointed in 1957 by the Minister of Housing and Local Government and is made up of representatives from water authorities, interested government departments and industry; condensed phosphates for use in detergents and possible replacements for these fall within the terms of reference of this committee and are kept under review.

van Wazer: Throughout the world politicians generally do what public opinion believes is correct. But on this issue, as I mentioned (p. 282), public opinion seems to be confused if not downright incorrect. An important function of science is to clarify to the public what scientists or technologists view as the controlling factors in a particular situation, but somehow we are not making a good job of this.

Alexander: How can decisions be made on a scientific basis when reputable scientists do not agree amongst themselves? Somebody has to make a decision.

R. J. P. Williams: All we can do is to put forward the maximum amount of information based on science, even if it is diverse. For most of the pollution problems that have come up so far the scientists have not been able to give a

quick solution but only to pool a mass of information. In democratic societies emotional values confuse these facts and many issues end up being decided through the ballot box, before the scientific evidence is complete. We have to accept that.

van Wazer: Mr Alexander reflects a popular misconception that scientists should speak with a single voice. The public should learn that, as different experts may emphasize different contributory factors, their conclusions may be diametrically opposed. The best approach is to lay all the evidence in front of the public (i.e. the underlying physical and economic factors of the case) as well as to state personal conclusions. Scientific papers are traditionally divided into sections such as 'Experimental Procedures', 'Results', 'Discussion' and 'Conclusions'; the public should be exposed more to the experimental procedures and results and not just to the conclusions.

Gilbert: If decisions such as whether to ban phosphates from detergents are to be taken eventually on political grounds let us recognize that there will be scientific disagreement and beg that those decisions are not too rushed, that plenty of time is allowed for debate. Dr Brydges commented on the role of industry in this debate. Industry has a duty to put its case as forcefully as possible to ensure that, when decisions are taken, we are aware of all the possible divergent opinions and the evidence has been examined in detail. In this particular case, the major detergent formulators have no direct involvement in the production of tripolyphosphate; they are still in business in areas where a phosphate ban applies. There is no particular commercial advantage to the formulators to resist the change from tripolyphosphate if they believe there are good reasons for such a change and if satisfactory substitutes are available. Moves toward replacement of phosphates have been slow because substitutes are not yet available that are satisfactory in all aspects of commercial performance and safety.

Brydges: Which aspects do you think we are missing in Canada, performance or safety?

de Oude: Canada does not have *zero*-phosphate legislation. Nitrilotriacetic acid, which is used in Canada, has proven to be satisfactory in the local conditions. At the same time the Canada Centre for Inland Water is closely surveying concentrations in environmental and drinking water for added reassurance.

Gilbert: The detailed monitoring exercise undertaken in Canada reflects a degree of uncertainty. But, just as the management of a body of water should vary in each particular case, so the risks involved in the use of a substitute for phosphate will vary from country to country, from case to case. Also the effectiveness of the replacement relative to the performance of the products

will vary from country to country since there are significant differences in washing habits.

Tinker: What is the level of uncertainty in this? We are all now clear that the decision on what level of eutrophication is acceptable in any place is subjective and political. The degree of eutrophication must also depend on the phosphorus concentration in different localities (i.e., on the temperature, the other components in the water and so on). However, did you mean, Mr Alexander, that even for the same body of water scientists do not agree about the effects of a given level of phosphate input?

Alexander: Scientists have disagreed for years about the effect of various concentrations of phosphorus in the input on Lake Erie, for instance. As Dr Brydges described, only a few years ago scientists were valiantly arguing that nitrogen and carbon, not phosphorus, were growth-limiting. Projections of what will happen in Lake Erie as the input varies contradict each other (i.e. those of G. F. Lee from Dallas and the Canadian group at the Canada Center for Inland Water). It always seems that those people who are consultants to one particular group come up with similar answers, those that are members of government research committees come up with another set of answers, and those who have no connection with either frequently come up with a third set!

Tinker: Are the figures in the Position Paper for the effect of phosphorus concentration on chlorophyll *a* content, Secchi-disc depth and so on generally accepted?

Alexander: Those data (and the whole paper) were circulated in draft form to members of the soap and detergent industry research committee, some government agencies and independent scientific members of the academic community. The published data are those agreed on by the majority. Some people do not agree with them.

de Oude: The Vollenweider model is generally accepted, although its applicability to reservoirs still needs confirmation. The main disagreement is usually about the contribution of factors affecting the input, such as concentration, flow, and lake characteristics.

Alexander: Even the Canadian and US Governments disagree about how accurate the Vollenweider model is. Region V's Position Paper is based on a more advanced model.

R. J. P. Williams: A clear message appears from the evidence as presented by Mr Alexander. The scientists involved in assessing The Great Lakes really failed: they failed to reach sufficient agreement and in the resulting atmosphere a political decision had to be taken, as in other areas of human endeavour, on the basis of satisfying the public. Exact parallels are seen in the development of nuclear power, coal resources etc. If we, as scientists, want to

influence decisions, we must learn to provide information in a way which does not confuse the decision-makers.

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Dr A. F. HARRISON studied Botany at London University (1961) and at the Waite Agricultural Research Institute, Adelaide, South Australia (for his Ph.D., 1966). Since 1967 he has been working in the Soils Subdivision of The Institute of Terrestrial Ecology (formerly the Nature Conservancy) in the UK specializing in phosphorus circulation in semi-natural ecosystems and phosphorus turnover in non-agricultural soils.

Professor T. D. INCH, D.Sc., is Superintendent of the Division of Organic and Physical Chemistry at the Chemical Defence Establishment at Porton Down and Visiting Professor at the Department of Pharmacy and Pharmacology of the University of Bath (UK). His research interests are phosphorus chemistry, synthesis of optically-active drugs and their use to explore biological reaction mechanisms, chemistry of metabolic processes, and carbohydrate chemistry.

Mr E. JOHNSTON graduated in Chemistry from Manchester University and joined Marchon Products Ltd. (now Albright & Wilson Ltd) in 1961. He worked in technical

service, production control, and from May 1970 until November 1976 was based in Italy with an Italian subsidiary company, latterly as export sales manager. Since returning to England, he has become Technical Relations Officer.

Mr M. KABBAJ after graduating in Physics (Paris) in 1962, was in charge of Mineral Processing, Technico-commercial, Geological and Mineral Processing Department of the *Office Cherifien des Phosphates* (Morocco) until 1975 when he became the Technical Research Director at the *Institut Mondial du Phosphate* in Paris.

Dr A. J. KIRBY is a Lecturer in Organic Chemistry at the University of Cambridge. His central research interest is reaction mechanism, particularly the mechanisms of reactions catalysed by enzymes. He is the author, with S. G. Warren, of *The Organic Chemistry of Phosphorus* (Elsevier, 1967).

Dr J.-F. LABARRE is Director of Research of the *Centre Nationale de la Recherche Scientifique* at the Laboratoire de Chimie de Coordination in Toulouse. Since gaining his doctorate (in the Physical Sciences) at that university he has developed his research interests on the application of quantum chemistry (e.g., to homogeneous catalysis and carcinogenesis) and has received several awards (including the Lomonossov medal from the University of Moscow in 1975).

Professor S. LARSEN, D.Sc., was Chief Soil Chemist at Levington Research Station of Fisons Ltd. (UK) from 1956 to 1972 and then was appointed Professor of Soil Fertility and Plant Nutrition at the Royal Veterinary and Agricultural University in Copenhagen in 1972. His main research is on phosphorus in soil and plants.

Dr B. D. LOUGHMAN is a Fellow of University College, Oxford, and University Lecturer in Agricultural (Plant) Science and currently Chairman of the Faculty Board of Biological Sciences. He was Botanical Secretary of the Society for Experimental Biology and Honorary Secretary of the Biological Council. His major publications are concerned with phosphorus utilization, the role of boron, polysaccharide synthesis and herbicide metabolism in higher plants.

Dr G. H. McCLELLAN after graduating in Geology and Physics, took a M.Sc. (University of Florida) in Geology-Metallurgical Engineering and a Ph.D. (University of Illinois) in Mineralogy-Crystallography-Chemistry. After doing research at the Universities of Illinois and Bordeaux (France) and for the Tennessee Valley Authority, he was appointed in 1976 as Geologist to the Technology Division of the International Fertilizer Development Center (Alabama), evaluating raw materials for use in the fertilizer processes and developing data files on raw materials for the Center's World Fertilizer Information System.

Dr W. M. NICOL is General Manager, Group Research and Development, and Programme Director, Food and Agriculture with Tate & Lyle, Ltd. (UK). Although for many years primarily engaged on studies of sugar he has broad interests in the food industry. A physicist by profession, he has had wide experience with Rolls Royce, British Oxygen and the Central Electricity Generating Board.

Dr H.-D. NIELEN studied Chemistry in Münster and Giessen from 1960 to 1969, when he joined Hoechst AG – Werk Knapsack. After working in the Inorganic Research

Department, since 1976 he has been Group Leader in the Technical Application Department. His fields of activity cover phosphorus chemistry and raw materials for detergents.

Mr N. W. Pirie, FRS, worked in Cambridge on the metabolism of methionine, glutathione and other sulphur compounds, on *Brucella* antigens and plant viruses before moving to Rothamsted in 1940 where he worked on the physiology of plant virus infection and on the extraction of leaf protein and its use as a human food. His publications include *Food Resources* (Penguin, 2nd edn. 1976) and *Leaf Protein* (Cambridge University Press, 1978). In 1976 he received the Rank Prize for Nutrition.

Dr C. S. Reynolds graduated in Zoology at the University of London and worked for his Ph.D. there on phytoplankton ecology. He joined the staff of the Freshwater Biological Association in 1970, since when he has worked on phytoplankton growth and population dynamics in eutrophic lakes.

Professor R. A. Shaw, D.Sc., studied organosilicon chemistry for his Ph.D. at the University of Leicester and then moved to Birkbeck College, London, as an Assistant Lecturer. He was promoted to Professor of Chemistry in 1965. His research interests are centred mainly on the chemistry of the non-metals. He was awarded an Honorary Doctorate by the University Paul Sabatier of Toulouse in 1977.

Dr P. B. Tinker obtained his Ph.D. at Sheffield University for work on tropolone compounds. After a year at Rothamsted, he spent seven years working at the West African Institute for Oil Palm Research, on problems of soil and plant nutrition, and three years working on sugar beet at Broom's Barn Experimental Station. For six years he lectured at Oxford University and in 1971 became Professor of Agricultural Botany at the University of Leeds. In 1977 he became Head of the Soils and Plant Nutrition Department at Rothamsted. His interests are soil–plant relationships, plant nutrition, and mycorrhizas.

Dr J. R. van Wazer took his Ph.D. at Harvard and is now Professor of Chemistry at Vanderbilt University, a position he has held for the past 10 years after spending 26 years in industrial research. From 1951 to 1963, he directed the research on phosphorus derivatives at the Monsanto Company. More than half his scientific publications (over 300) deal with various aspects of phosphorus chemistry.

Mr J. H. Williams is Regional Soil Scientist in the West Midland Region of the Agricultural Development and Advisory Service of the UK Ministry of Agriculture, Fisheries and Food. After graduating in Chemistry at the University of Wales in 1951 he researched into the effects of molybdenum on the productivity of upland pastures. He has spent the past 25 years as a Soil Scientist in the Ministry of Agriculture. His special interests include soil phosphorus, pesticides and pollution.

Professor R. J. P. Williams, FRS, is the Napier Royal Society Research Professor at the Inorganic Chemistry Department, Oxford (UK). His major interests are the involvement of inorganic elements in living systems, the use of nuclear magnetic resonance spectroscopy in the study of biological systems both *in vitro* and *in vivo*, and bioenergetics.

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